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(1596—1650)

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Recombination of Gaseous Ions

By H. S. W. MASSEY, F.R.S.

University College, London

§1. INTRODUCTION

THE study of recombination between ions dates back to 1897 but we are still far from possessing a thorough understanding of the nature of all the processes involved. In recent years attention has been drawn to the subject because of the importance of recombination in limiting the ionization concentration which can be achieved in a large volume with a given ionizing source. This applies particularly to the ionized layers of the upper atmosphere—the ionosphere—which play such an important part in radio propagation, as well as to a gaseous discharge at high pressure when loss by diffusion to the walls is small. Recombination also plays an important part in determining the properties of the outer regions of the solar atmosphere, particularly the solar corona. We shall be mainly concerned in this review with recombination processes occurring in gases at pressures below atmospheric.

The rate of recombination is usually specified in terms of the recombination coefficient α which is such that, if n^+ , n^- are the respective number of positive and of negative ions per cubic centimetre and there is no source of ionization present, then, due to recombination,

$$\frac{dn^+}{dt} = \frac{dn^-}{dt} = -\alpha n^- n^+. \quad \dots \dots \dots (1)$$

It is important to remember that with this definition α may be found to depend on n^+ or n^- or both. We shall distinguish at the outset between recombination between positive ions and electrons and between positive ions and negative ions. Both the nature of the processes and the experimental techniques for observing them are quite different.

Although there is still little information about the rate of recombination of positive and negative ions at low pressure there has been a very substantial clarification of electron-ion recombination in the last two

years due to the application of microwave techniques to the experimental study of the problem. We shall first discuss the present knowledge of the mechanism of electron-ion recombination derived both from theory and experiment, and then give a brief account of the state of knowledge of recombination between ions at pressures below atmospheric. The concluding sections will be devoted to a short discussion of applications to the ionosphere and the solar corona.

§ 2. ELECTRON-ION RECOMBINATION

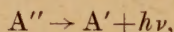
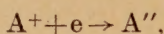
2.1. *Possible Recombination Processes*

When two charges recombine energy must be released in some form. In electron-ion collisions the following possibilities arise.

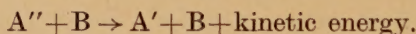
(a) *Radiative recombination.* The surplus energy is released as radiation viz. :—



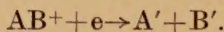
(b) *Dielectronic recombination.* In a process of this kind the surplus energy is given to a second electron in the positive ion so that a doubly excited atom is initially formed. This is unstable towards auto-ionization but may be stabilized by collision or by radiation. The sequence is therefore :—



or

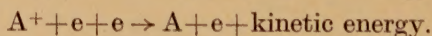
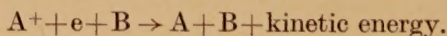


(c) *Dissociative recombination.* If the positive ion is molecular the surplus energy may be absorbed in dissociating the molecule viz. :—



As we shall see this process appears to be a very important one in practice.

(d) *Three-body recombination.* The surplus energy may be taken up by a third body which is in the neighbourhood of the interacting charges. This third body may be a neutral atom or molecule, a positive ion or an electron, the reactions being :—



Apart from wall recombination, which is an extreme case of (d), no other processes seem possible. We shall first give a theoretical summary of the expected importance and magnitude of the recombination coefficients arising from each of these five possibilities and then proceed to examine the experimental evidence.

2.2. *Radiative Recombination*

The recombination coefficient for the simplest process of this kind, the recombination of electrons with protons, can be calculated to a very

high accuracy. However, as account must be taken of the possibility that the electron may be captured into any excited state as well as the ground state, the calculation is very tedious.

The most detailed calculations have been carried out by Bates, Buckingham, Massey and Unwin (1939). They used the standard form for the cross section for radiative capture of an electron from a free to the n th bound state.

$$Q_n = \frac{64\pi^4\nu^3\epsilon^2}{3hc^3\nu} \left| \int \psi_i^* \mathbf{r} \psi_n d\tau \right|^2, \quad \dots \quad (2)$$

where ψ_n is the wave function of the bound state, normalized as usual, and ψ_i is that for the initial 'free' state normalized to have the asymptotic form of a plane wave (apart from the logarithmically varying phase factor due to the Coulomb field) of unit amplitude and the corresponding scattered wave, ν is the initial velocity of the electron and ν the frequency of the emitted radiation.

To calculate the radiative recombination coefficient α_r it is necessary to sum over all final states n to give

$$\alpha_r = \nu \sum_n Q_n. \quad \dots \quad (3)$$

If the calculations are carried out in spherical polar coordinates the summation is actually a double one since the cross section will depend not only on the principal quantum number of the final state but also on the azimuthal quantum number l . The double summation may be avoided by working in parabolic coordinates as first pointed out by Oppenheimer (1929). It is then found that

$$Q_n = q_u^n + q_z^n$$

where

$$\left. \begin{aligned} q_u^n &= A \frac{32n^2\lambda^{10}}{(n^2+\lambda^2)^4} \sum_{s=0}^{s=n-2} (s+1)(n-s-1) \\ &\quad \left| F\left(1-i\lambda, 2+s-n, 2, -\frac{4in\lambda}{(n-i\lambda)^2}\right) \right|^2, \\ q_z^n &= A \frac{\lambda^6}{(n^2+\lambda^2)^2} \sum_{s=0}^{s=n-1} \left| (n-s-1)F\left(-i\lambda, 2+s-n, 1, -\frac{4in\lambda}{(n-i\lambda)^2}\right) \right. \\ &\quad \left. - \left(n-s-1-\frac{2in\lambda}{n+i\lambda}\right)F\left(-i\lambda, 1+s-n, 1, -\frac{4in\lambda}{(n-i\lambda)^2}\right) \right|^2, \\ A &= (8h^4\nu/3\pi m^3\epsilon^2c^3) \operatorname{cosech} \pi\lambda \exp \{\pi\lambda - 4\lambda \arctan n/\lambda\}, \\ \lambda &= 2\pi\epsilon^2/h\nu. \end{aligned} \right\} \quad \dots \quad (4)$$

and $F(a, b, c, z)$ is the usual hypergeometric function.

Using these formulae Bates, Buckingham, Massey and Unwin evaluated Q_n for low electron energies for values of n as high as 40. This was rendered practicable by the use of the recurrence relation:

$$(c-b)F(a, b-1, c, z) = b(1-z)F(a, b+1, c, z) \\ + \{(a-b)(1-z) + (c-b-a)\}F(a, b, c, z).$$

Results obtained for the contributions to the recombination coefficient for different values of the quantum numbers are given in table 1 for electrons with energies ranging from 0.034 to 0.28 ev.

Table 1. Recombination of Electrons with Protons—Contributions from Radiative Capture to Various Excited States

Electron Energy Total q.no. of final state	ev Azimuthal q.no. of final state	0.28	0.13	0.069	0.034
		Recombination coefficient in 10^{-13} c.c./sec			
1	0	2.54	3.54	5.12	7.30
2	0	0.38	0.52	0.75	1.07
	1	0.95	1.38	2.01	2.91
3	0	0.13	0.18	0.25	0.36
	1	0.36	0.53	0.77	1.10
	2	0.36	0.56	0.85	1.25
4	All l	0.59	0.91	1.38	2.03
5	"	0.43	0.68	1.07	1.62
6	"	0.31	0.53	0.86	1.34
7	"	0.23	0.43	0.70	1.12
8	"		0.35	0.59	0.96
9	"		0.28	0.50	0.82
10	"		0.22	0.43	0.71
12	"			0.31	0.55
14	"			0.23	0.44
16	"				0.36
18	"				0.29
20	"				0.23
$\sigma = \sum_{n=1}^{\infty} \alpha_n$		7.2	11.4	18.6	29.7

For some purposes it is of interest to examine the dependence of the capture cross section on the azimuthal quantum number. This may be done by working in spherical polar coordinates, following Morse and Stueckelberg (1930) and Wessel (1930). Some typical results are included in table 1 which indicates that the largest contribution for a given n comes from values of $l \simeq n$.

It will be seen from table 1 that the convergence of the series is quite slow so that in a recombination spectrum transitions from highly excited states should be strong, as is found. The total recombination coefficient is seen to be quite small even at the lowest electron energy concerned, although the rate of increase with decreasing electron velocity is quite rapid.

The extrapolation of the results for protons to apply to recombination with other positive ions is not difficult, unless very high accuracy is required. An important case is that of recombination to O^+ ions as these are prominent in the ionosphere. For most excited states the behaviour will be very nearly the same as for hydrogen and the only important modification necessary will be in the contribution from capture to the ground state. The cross section for capture by a bare ion of charge $+Ze$ is Z^2 times that for capture by a proton but it is

dangerous to attempt to use this to estimate the appropriate cross section for capture by a positive ion of charge $+\epsilon$ to which several electrons are already bound. Thus one might argue that the effective nuclear charge acting on an electron in the 2p-shell of oxygen is about 3 and therefore the cross section for capture into a 2p-orbital of oxygen should be about nine times that for capture into the 2p-orbital of hydrogen. It has been pointed out, particularly by Bates (1939), that this method of estimation not only fails to give the correct variation of capture cross section with electron energy but also may be grossly incorrect as far as absolute magnitude is concerned.

Bates (1946) has shown that a much better approximation is to use, for the free wave function ψ_i , just that for motion in the field of a charge $+e$ unmodified by the presence of an inner core. In this way he has calculated the cross sections for continuous absorption of radiation by the atoms in the first row of the periodic table from lithium to neon. Since the cross section for capture into the ground state is the inverse process, the contribution to recombination into the ground state may be obtained from Bates' results by application of the principle of detailed balancing.

For certain atoms, particularly oxygen and neon, detailed calculations (Seaton 1951 a) have been carried out in which Hartree-Fock wave functions have been used for the ground state wave function of the atom and the 'free' wave functions have been obtained by numerical integration of the wave function for the motion of the electron in the Hartree-Fock field of the ion. Table 2 gives the values obtained for

Table 2. Radiative Recombination Coefficients for Oxygen

Temperature (° K)	α in 10^{-12} c.c./sec		
	Contribution from ground state	Contribution from excited state	Total
8000	0.035	0.189	0.224
4080	0.048	0.331	0.379
2000	0.069	0.614	0.683
1020	0.096	1.07	1.17
500	0.138	1.84	1.98
222	0.207	3.13	3.34

the radiative recombination coefficient to atomic oxygen. The calculations of Bates and Seaton (1949) have been used to give the contribution from the ground states and those from higher states have been assumed to be as for hydrogen (see table 1). The initial electron energies E are given in terms of a temperature T defined by $T=E/k$. It will be seen that the total radiative recombination coefficient remains low for these atoms and it seems to be quite definite that this will hold for all atoms. As a rough rule the order of magnitude is never likely to exceed $10^{-11}/\text{cm}^3/\text{sec}$ for thermal electrons.

For reasons which will be clear later it is important to examine the likely accuracy of the theory. The formula (2) for the capture cross section can certainly be relied upon to give accurate results if the wave functions ψ_i and ψ_n are accurately known. There also seems no doubt that the higher excited states of atoms can be treated as hydrogen-like with sufficient accuracy. This leaves only the question of whether any gross error is likely to be committed in calculating the contribution from capture to the ground state. A glance at table 2 shows that, to increase the value of the total radiative recombination coefficient for oxygen by a factor of 10, the calculated value for the ground state would have to be increased by a factor of 70 or so. An error of this magnitude and in this sense is extremely unlikely. Examination of the degree of overlap between the approximate functions ψ_i and ψ_0 (the ground state function) used for oxygen shows that it is quite large and could not be increased to provide a very much greater value for the integral in (2). Similar considerations apply to neon and it is hoped in this case that direct experimental check will be possible from observation of the continuous absorption coefficient of neon for short wave radiation.

Some doubt was originally cast on the validity of the theory by the observations of the continuous absorption coefficient of potassium made by Ditchburn, Tunstead and Yates (1943). The observed coefficient is very low near the limit and exhibits a minimum at a wavelength of about 2700 Å. The first theoretical attempts (Phillips 1932) to reproduce this behaviour were unsuccessful but a later investigation by Bates (1947) showed that, in this case, a very severe cancellation occurs in the integrand in the dipole matrix element so that extreme accuracy would be required in the wave functions to give the correct cross section. By introducing a variable polarization parameter to allow for the effect of polarization of the ionic core by the free electron, and calculating cross sections for various values of this parameter, Bates was able to show that the observations could be quite well understood in terms of the theory.

A further detailed theoretical study of the absorption coefficients of the four alkali metal atoms, Na, K, Rb and Cs has been carried out by Seaton (1951 b). For sodium the main features observed by Ditchburn and Jutsum (1950) were reproduced by the theory in which Hartree-Fock functions were used for both the initial and final wave functions. When allowance was made for spin-orbit coupling the finite minimum observed definitely in the variation with frequency of the absorption coefficient of caesium (Mohler and Boeckner 1929, Braddick and Ditchburn 1934) and indicated also from the less extensive observations in rubidium (Mohler and Boeckner 1929, Lawrence and Edlefsen 1929) could be explained to within the accuracy of the observations. The considerable degree of success achieved in reproducing theoretically the observed features of the absorption by the alkali metal atoms, for all of which the problem is rendered difficult by the strong cancellation in the transition

matrix element, makes one feel confident that for atoms in which the degree of cancellation is much less the theoretical results are certainly accurate to much more than an order of magnitude.

Some experimental evidence in support of the calculated capture cross sections has been obtained by Mohler (1933). The method used is to determine the intensity of the continuous spectrum emitted from the positive column of an arc discharge in caesium vapour. If at the same time the electron concentration and temperature are measured and the source of the radiation identified as due to capture into a particular state, the corresponding capture cross section may be determined. Mohler investigated the intensity in the neighbourhood of the 6p limit and assumed that it was due to radiative capture to the 6p level. Various checks were applied to verify that the observed radiation was due to this capture process. A capture cross section of $1.7 \times 10^{-21} \text{ cm}^2$ was found for 0.3 ev electrons. Reference to table 1 shows that this is of the order of magnitude expected from the theory.

Radiative capture is an important process in many astrophysical phenomena. A brief account is given in §6 of its application in certain aspects of the theory of the solar corona.

2.3. Dielectronic Recombination

The possible importance of this process, which is one of inverse auto-ionization, was first suggested by Sayers (1939) and an estimate of the corresponding recombination coefficient has been given by Massey and Bates (1943).

Let $n(E) dE$ be the number of free electrons per unit volume, with energy between E and $E + dE$. The cross section for capture of an electron into a doubly excited state with energy E_s above that of the ground state of the ion is then given by (Bloch and Bradbury 1935)

$$Q_c = w_1 \frac{4\pi^2}{h\nu} n(E_s) |M|^2, \quad \dots \dots \dots (5)$$

where w_1 is the statistical weight of the doubly excited state, ν is the speed of the electrons corresponding to the energy E_s , and M is the transition matrix element of the interaction between the electron and the ion which makes the process possible. The rate at which the doubly excited atom will break up again into ion and electron is also proportional to $|M|^2$, the life-time θ towards auto-ionization being given by

$$\theta = \frac{h^4}{16\pi^3 w_2} \{(2m)^3 E_s\}^{-1/2} |M|^2, \quad \dots \dots \dots (6)$$

where w_2 is the statistical weight of the ground state of the ion. We therefore have

$$Q_c = \frac{w_1 h^3}{4\pi w_2 \nu} (2m)^{-3/2} E_s^{-1/2} n(E_s) / \theta. \quad \dots \dots \dots (7)$$

Recombination will only result if there is a finite chance that the doubly excited atom can stabilize itself by getting rid of its energy in some

other way. If τ_s is the life-time of the doubly excited state towards this stabilizing process the cross section for dielectronic recombination is given by

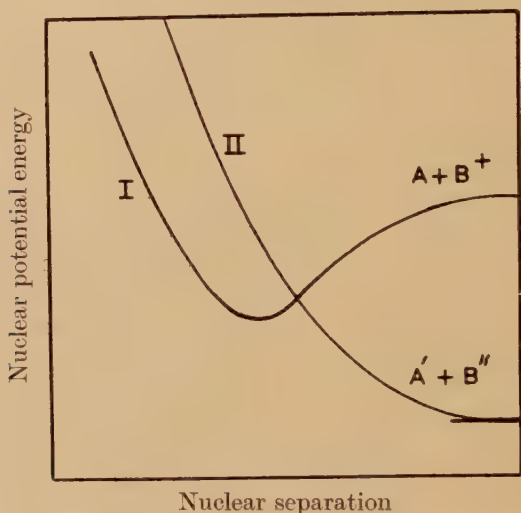
$$Q_d = \frac{\theta}{\theta + \tau_s} Q_c. \quad (8)$$

The recombination coefficient α due to this process is therefore given by

$$\begin{aligned} \alpha &= v Q_d \\ &= \frac{w_1 h^3}{4\pi w_2} (2m)^{-3/2} E_s^{-1/2} n(E_s) / (\tau_s + \theta). \quad (9) \end{aligned}$$

In practice the stabilizing process can only be one of radiation unless the gas pressure is very high. τ_s is therefore of order 10^{-8} sec, at least, whereas θ is of order 10^{-13} sec (Ta-You Wu 1944, Shenstone 1948).

Fig. 1



Illustrating the process of dissociative recombination.

For atoms such as helium this formula shows quite clearly that no important contribution to recombination of thermal electrons can come from this process as the doubly excited states lie so high. Even for more complicated atoms such as oxygen and neon, a study of the energy levels shows it is most unlikely that the coefficient of dielectronic recombination can greatly exceed 10^{-12} cm³/sec.

2.4. Dissociative Recombination

It is far more difficult to estimate the rate at which this process will occur with any particular molecular ion although Bates (1950 a) has been able to show that it is likely to occur at a much faster rate than either of the radiative processes described above.

The nature of the process may best be seen by reference to molecular potential energy curves. In fig. 1, curve I is the potential energy curve

for the ground state of a molecular ion AB^+ . This curve will intersect certain curves for states of the neutral molecule AB and some of these intersections (such as that with curve II in fig. 1) may occur at nuclear separations close to that in the normal state of AB^+ . At such an intersection the system $AB^+(\text{normal state}) + \text{electron}$ (with small kinetic energy) will be in energy of resonance with a repulsive state of the neutral molecule AB . Hence in a collision of a slow electron with the ion AB^+ a transition may occur to this latter state leading to two neutral and, in general, excited atoms A, B . Since the probability of this transition depends very much on the interaction occurring near the equilibrium separation of the molecular ion it is clear that estimation of the actual rate of reaction for any particular molecular ion will be very difficult. It seems probable even from this very qualitative examination of the process that, for some ions, it might yield a much larger recombination coefficient than any radiative process. In 1947 Bates and Massey, from an examination of ionospheric data, were led to conclude that dissociative recombination must be a dominant process in the ionosphere and, in 1950 Bates was able to show by the following argument that the dissociative recombination coefficient could indeed be several orders of magnitude greater than for radiative processes.

The process can be regarded in a similar way to dielectronic recombination but two differences must be allowed for in the formula (9). The initial capture is not confined to such a narrow electron energy range when allowance is made for nuclear vibration. A factor $f(E) dE$ determined by the overlap of initial and final nuclear vibrational wave functions must be introduced, this being such that

$$\int f(E) dE = 1$$

when the integration is taken over all possible vibrational transitions.

The second difference concerns the interpretation of τ_s . The neutral molecule formed by the electron capture will be in a repulsive electronic state so the nuclei will separate as long as the neutral system is stable. Once the separation becomes large enough the chance of autoionization occurring to reverse the process will be small. τ_s can therefore be regarded as the time taken for the nuclear separation to become large enough for this to be so.

We now have, for the recombination coefficient, assuming the electrons have a Maxwellian velocity distribution about a temperature T ,

$$\alpha = \frac{w_1 h^3}{2w_2} (2\pi m k T)^{-3/2} \int \exp(-E/kT) f(E) \{\theta(E) + \tau(E)\}^{-1} dE. \quad (10)$$

Numerical substitution for the various constants gives

$$\alpha = 2.1 \times 10^{-16} \frac{w_1 T^{-3/2}}{w_2 (\bar{\theta} + \bar{\tau})} \int \exp(-E/kT) f(E) dE \text{ c.c./sec}, \quad (11)$$

where $\bar{\theta}$ and $\bar{\tau}$ are suitable mean values.

To obtain some idea of the possible magnitude of α we note that w_1/w_2 may be of order 10 if a number of repulsive excited states of the neutral molecule can contribute. $\bar{\theta}$, the mean life-time towards auto-ionization, is of order 10^{-13} sec (see § 2.3) and \bar{v} may be taken of the same order, for the velocity of nuclear separation is of order 10^5 cm/sec and a change in separation of 10^{-8} cm is very likely to reduce the chance of autoionization to negligible proportions. If the interactions occur very close to the normal nuclear separation in the ground state of the ion $f(E)$ will be large for small E and the integral will be of the order kT . Under these circumstances at room temperature the value of α comes out to be about 10^{-7} cm³/sec. The reason why this is about 10^5 times larger than the contribution from dielectronic recombination is simply that stabilization through nuclear separation is 10^5 times as rapid as that due to radiation.

The importance of dissociative recombination has been confirmed by the recent experimental work using microwave techniques (see § 3).

2.5. Three-body Recombination

We consider first the case in which the third body to which the surplus energy is communicated is a neutral atom or molecule. The theory of three-body recombination between ions under these conditions has been given in the now classic paper by J. J. Thomson (1924). A short account of J. J. Thomson's theory, which is well supported by strong experimental evidence, is given in § 4.1. According to this theory the three-body recombination coefficient, in a gas in equilibrium with ions and electrons at temperature T , is given at low pressures by

$$\alpha = \frac{64(2\pi)^{1/2}}{81} \frac{\epsilon^6}{(kT)^{5/2}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2} \left(\frac{1}{l_1} + \frac{1}{l_2} \right), \quad \dots \quad (12)$$

where M_1 and M_2 are the masses of the recombining ions and l_1, l_2 are the free paths for collisions between the respective ions and the gas atoms in which an amount of energy of order kT is transferred to the atoms. This formula is valid only when the masses M_1 and M_2 are both comparable to that of a gas atom. If one of the ions has a very small mass, as is the case in electron-ion recombination, the only effective collisions are those in which the light ion or electron gives up energy to the gas atoms. The appropriate free paths for collisions of this kind, in an atomic gas, in which an amount of energy of order kT is given up will be of order Ml/m where m is the mass of an electron, M of a gas atom and l the usual mean free path for elastic electron collisions in the gas. This means that in (12) we must put $1/l_1 = 0$, $l_2 = Ml/m$, $M_2 = m \ll M_1$, to give

$$\alpha \simeq \left(\frac{8kT}{\pi m} \right)^{1/2} \frac{8\pi r_0^3 m}{3M_1 l}, \quad \dots \quad (13)$$

where $r_0 = 2e^2/3kT$. This formula should give the correct order of magnitude provided the gas pressure is not so high that $r_0 \simeq Ml/m$.

If numerical values are substituted in the formula (13) the three-body recombination coefficient for electrons in helium comes out to be about

$10^{-11} p \text{ cm}^3/\text{sec}$ where the pressure p is given in mm of mercury. This should hold up to pressures of over 30 atmospheres. In a molecular gas somewhat higher values might be expected due to the possibility of an electron losing energy to a gas molecule by exciting vibration. This could decrease the free path l by an appreciable factor. Thus for air, using the data from the most recent electron diffusion experiments of Huxley and Zaazou (1949) to estimate the mean loss of energy on collision of an electron with an air molecule, the three-body recombination coefficient might be as large as $2 \times 10^{-10} p \text{ cm}^3/\text{sec}$ at pressures below 20 atmospheres.

It appears that, at pressures below 0.1 mm Hg three-body processes are even less effective than radiative ones in producing recombination.

In a dense plasma there may be important effects arising from three-body collisions between charged particles. Such collisions, in which two electrons and one ion are involved, might well lead to recombination as one electron could readily give up much of its initial energy to the other so making possible its capture by the ion. The process would be the inverse of ionization of a highly excited atom by impact of a slow electron, and in a recombining plasma such ionization processes would also proceed at the same time as the recombination. The effective rate of recombination would depend on the gradual change in the equilibrium between the capture and the ionization processes. It has proved very difficult to obtain even semi-quantitative estimates of the importance of these processes. Owing to the long range of the Coulomb interaction and the corresponding gradual character of the process the Thomson theory is not really applicable, but it does seem at least probable that recombination arising in this way will decrease much more rapidly with increasing electron temperature than with any other recombination process. This is because of the rapid decrease in the intensity of Coulomb scattering with the relative velocity. It is important to bear in mind that, in a dense plasma, at a low electron temperature, the effects might be quite important but should show up in an increase of the recombination coefficient with electron concentration.

§ 3. THE EXPERIMENTAL INVESTIGATION OF ELECTRON-ION RECOMBINATION

3.1. *Principle of the Method*

The obvious method of studying electron-ion recombination experimentally, at low pressures, is to investigate the rate of decrease of electron concentration n_e in a discharge afterglow. There are two principal ways in which electron removal occurs, through ambipolar diffusion to the walls and by recombination. The first of these predominates at very low pressures, the second at higher pressures. It is possible to test which, if either, is dominant under any particular conditions by examining the n_e -time relation. If recombination is alone important

$$\frac{dn_e}{dt} = -\alpha n_e^2$$

so, if n_1, n_2 are the electron concentrations at times t_1 and t_2 respectively

$$\frac{1}{n_2} - \frac{1}{n_1} = \alpha(t_2 - t_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

i.e. a linear relation between $1/n$ and t whose slope is the recombination coefficient.

The n_e-t relation is quite different when ambipolar diffusion is the effective removal process. If D_a is the ambipolar diffusion coefficient then

$$-D_a \nabla^2 n_e + \frac{\partial n_e}{\partial t} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

For a spherical container of radius R

$$-D_a \frac{d^2}{dr^2} (rn_e) + \frac{\partial (rn_e)}{\partial t} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

with $n_e=0, r=R$. This gives

$$n_e = r^{-1} \sum_{s=1}^{\infty} a_s \sin(s\pi r/R) \exp \{-s^2 \pi^2 D_a t/R^2\}, \quad . \quad . \quad . \quad (17)$$

where the a_s depend on the distribution of ionization within the container at the instant the discharge is cut off. If the ionization rate when the discharge is on, is nearly uniform through the container a_1 will be larger than the remaining a_s so, a short time after the discharge is cut off, the density will decay exponentially as $\exp \{-\pi^2 D_a t/R^2\}$. In this case $\log n_e$ will vary linearly with t at a rate which determines D_a . D_a is given in terms of the diffusion coefficients D_e, D^+ and mobilities k_e, k^+ of electrons and positive ions respectively, by

$$D_a = (D^+ k_e + D_e k^+) / (k^+ + k_e). \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If the plasma is in thermal equilibrium with the gas during the decay period $D^+/k^+ = D_e/k_e = kT/\epsilon$ and $k_e \gg k^+$ so that

$$D_a \simeq 2D^+. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

It follows that, if the $\log n_e-t$ plot is linear, the diffusion coefficient and mobility of the positive ions in the afterglow may be obtained from the slope of the plot.

In fact there are circumstances in which the n_e-t relation is more complex than given by either the recombination or diffusion law or by allowance for both. Further reference to such cases is made in § 3.4 below.

3.2. Measurement of Electron Concentration in an Afterglow

Experimental techniques depend on the methods used for measuring n_e as a function of t in an afterglow.

In the earlier measurements n_e was determined by optical or by electrical probe methods. Thus in Mohler's experiments (1937 a) in caesium vapour two optical methods, one depending on visual intensity measurements, the other spectrophotometric, were used as well as a probe method.

The visual intensity method rests on the assumption that the intensity of light emitted from the afterglow varies as n_e^2 . In Mohler's work the total intensity I of light emitted by the afterglow in a 7×10^{-4} sec interval was measured photometrically at different intervals after the discharge was short circuited. It was found that, under many experimental conditions $I^{-1/2}$ varied linearly with t as expected if the initial assumption is valid and the electron density falls off according to a recombination law.

Total optical intensity measurements have also been carried out in recent investigations. The technique (Holt, Richardson, Howland and McClure 1950) has been to measure the total intensity emitted using a photomultiplier tube, together with suitable optical filters to compare the observations at different wavelength regions. By a suitable delay circuit it is possible to arrange that the photomultiplier is only sensitive at the time at which the observation is required.

The spectrophotometric method depends on a comparison of the intensity of the recombination spectrum of the afterglow with the same spectrum in a steady state. The interpretation of the data in terms of electron concentration is much more involved than for the total visual intensity observations. In recent work (Holt, Richardson, Howland and McClure 1950) the spectrum of the afterglow has been examined at different times after discharge cut-off.

The processes leading to emission of light, in the afterglow may be so much more complex than at first thought that the evidence from optical measurements can only be regarded as complementary to that obtained by use of electrical methods.

Probe methods employ the technique of the Langmuir probe to measure the electron concentration. It is well known that great care must be exercised in interpreting probe data, particularly when the probe is used with potential below that of its surroundings. The latter arrangement was found to be necessary by Mohler in his investigation of the decay of electron density in caesium and mercury afterglows (1937 b), as reproducible results could not be obtained when the probe was used in the conventional way, i.e. positive to the surrounding space. Although Mohler attempted to correct for these difficulties, the probe measurements cannot be regarded as wholly reliable indications of the electron concentration in these experiments. It is clear that any future use of probe methods for investigation of recombination in an afterglow must be preceded by a thorough study of the reliability of the method for this purpose, as undertaken by Sayers.

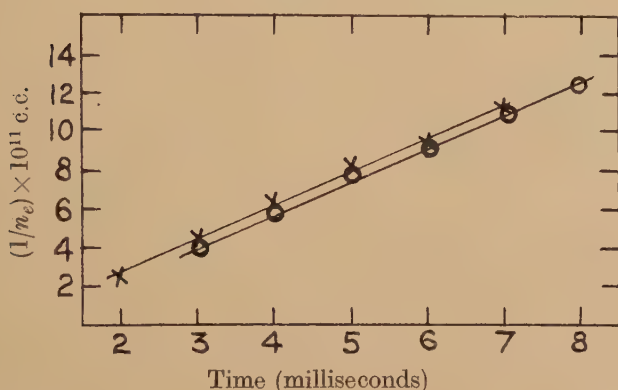
The development of microwave techniques has now made available a much more convenient and reliable method for determining the electron concentration at any instant in the afterglow. The principle of the method is the measurement of the change of frequency of a resonant cavity enclosing a vessel in which the discharge can be initiated and then cut off at suitable intervals. The change $\Delta\nu$ in frequency of such a

is to be compared with 21.4 cm/sec per volt/cm measured by Tyndall and Powell (1931) and 12 cm/sec per volt/cm calculated by Massey and Mohr (1932) for the mobility of He^+ ions in helium. The observed ambipolar diffusion coefficient was found to be proportional to $1/p$ for pressures p up to 11 mm Hg.

The interpretation of these results was not at first obvious. The recombination coefficient found is about 10^4 times greater than that calculated for radiative recombination. The pressure is far too low for three-body processes to be effective and the gas is monatomic so that processes involving molecules would appear at first sight to be also ruled out. However, it was pointed out by Bates (1950 b) that the molecular ion He_2^+ is stable and, under the experimental conditions, would be produced by three-body collisions such as



Fig. 2



Variation of reciprocal electron concentration ($1/n_e$) with time after cutting off a discharge in pure helium.

○ exptl. points at a pressure of 28.7 mm Hg.

× exptl. points at a pressure of 21.2 mm Hg.

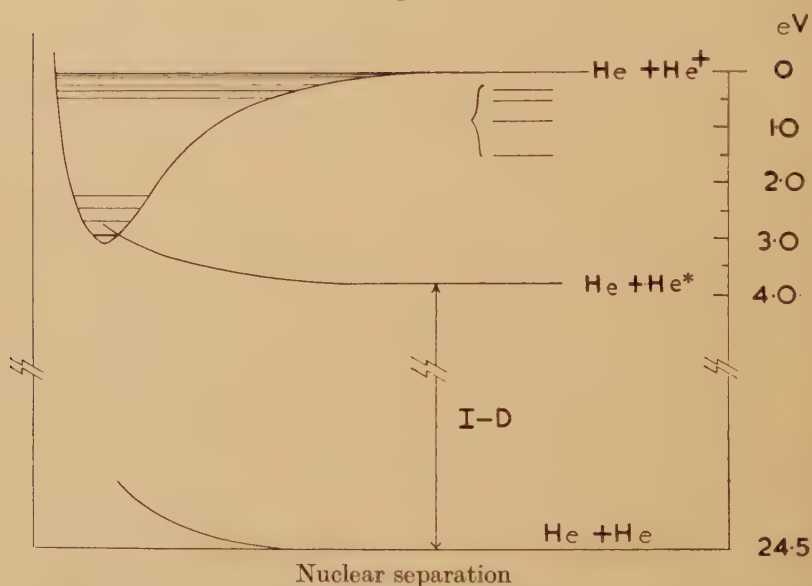
at such a rate that a considerable proportion of the positive ions in the afterglow should be He_2^+ . In that case the recombination process could be the dissociative one



The importance of He_2^+ ions in a helium discharge was shown shortly after by Boyd (1950) who applied the time-of-flight analyser, which he had developed for studying the ionic constitution of discharge plasmas, to an arc discharge in helium at a pressure of 0.01 mm Hg, the discharge current being 100 mA, and found that 70% of the ions were He_2^+ . If such a high proportion is possible while the discharge is actually operating it is likely to be very great in the afterglow.

Biondi and Holstein (1951) attempted to throw fresh light on the problem by simultaneously measuring the electron density and the intensity and spectral distribution of the radiation emitted by the afterglow. If the recombination process is a dissociative one involving He_2^+ ions in the ground vibrational state the dissociation (22) can give rise at most to excited atoms in which the excitation energy is $I-D$ where I is the ionization energy of He and D the dissociation energy of He_2^+ (see fig. 3). D has been estimated theoretically by Pauling (1933) and Weinbaum (1935) and from molecular spectra by Herzberg (1950) as lying between 2.2 and 3.1 eV. Nevertheless Biondi and Holstein found lines in the afterglow spectrum originating from atomic levels only between 0.3 and 1.5 eV below the ionization limit. The observation.

Fig. 3



Potential energy curves for He_2^+ and He_2 illustrating the need for vibrational activation in order to interpret observed spectra in a helium afterglow in terms of dissociative recombination. Upper limits of observed helium lines are indicated by the bracket.

that roughly one quantum of variable radiation is emitted for each electron lost by recombination indicates strongly that the emission is directly associated with the recombination process. At first sight the evidence would appear to be against Bates' interpretation but it must be remembered that there is no reason why the He_2^+ ions should be formed in their ground vibrational states. Dissociative recombination to He_2^+ ions possessing a high degree of vibrational excitation would lead to excited atoms with a sufficient degree of excitation. It was estimated by Biondi and Holstein that, if this is correct, in their experiments the

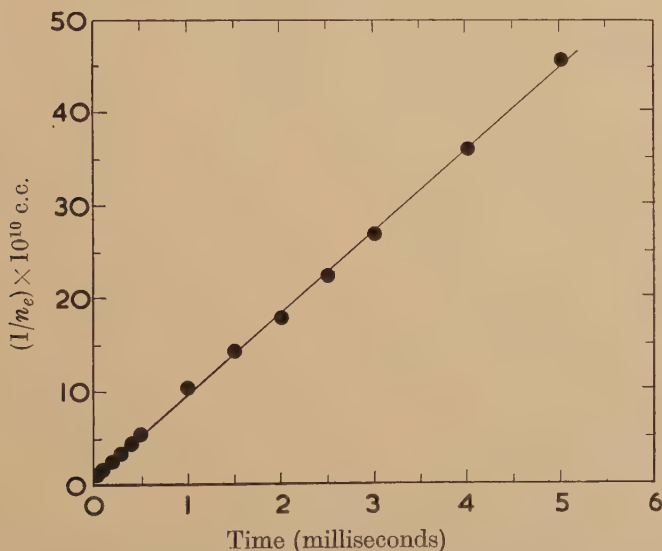
vibrational excitation must have persisted through 10^6 collisions. This is not impossible as it is well known that vibrational deactivation by collision is often very ineffective (Massey and Burhop 1952).

Much more decisive evidence was probably produced in a remarkable experiment suggested by Biondi and Holstein and carried out by Biondi (1951 a). It has long been known that the Townsend ionization coefficient of helium may be changed very considerably by the admixture of a very small proportion of argon. This has been ascribed to the reaction



where He' denotes a metastable helium atom. Biondi therefore investigated the rate of electron decay in a helium afterglow containing 0.1% of argon in the hope that the ions would be mainly A^+ . With the small concentration of argon present the rate of production of A_2^+ ions should be negligible while He A^+ is probably not very stable, if at all.

Fig. 4



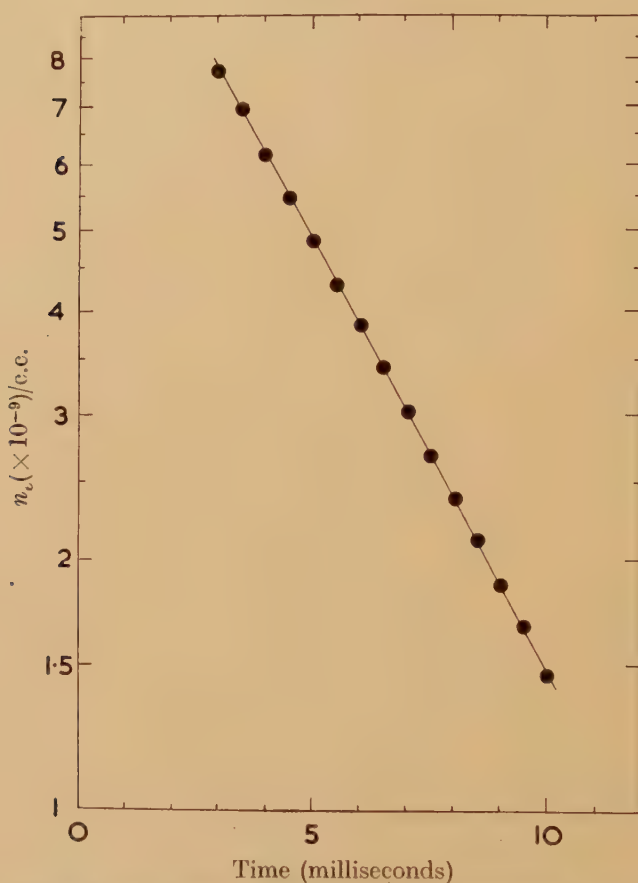
Variation of reciprocal electron concentration ($1/n_e$) with time after cutting off a discharge in pure argon at a pressure of 14 mm Hg.

The stability of molecular ions such as He_2^+ must be largely due to resonance between the structures HeHe^+ , He^+He , an effect which is absent in a heteronuclear molecular ion.

The experimental results completely justified all expectations and seem to confirm that the large recombination coefficients are entirely due to the dissociative process suggested by Bates. In pure argon at 14 mm Hg pressure the large value of 8.8×10^{-7} c.c./sec was found for α , the linear plot of $1/n_e$ against t being as illustrated in fig. 4. On the other hand at 7 mm Hg pressure in helium containing 0.1% of argon

no loss by recombination could be detected, the loss being due almost entirely to diffusion. This is illustrated in fig. 5 in which $\log n_e$ is shown to vary linearly with t . The accuracy of the observations is such that the recombination coefficient in this afterglow must be $< 8 \times 10^{-10}$ c.c./sec. Furthermore, the measurement of the total intensity of radiation emitted by the afterglow when 0.1% of argon was mixed with helium was found

Fig. 5



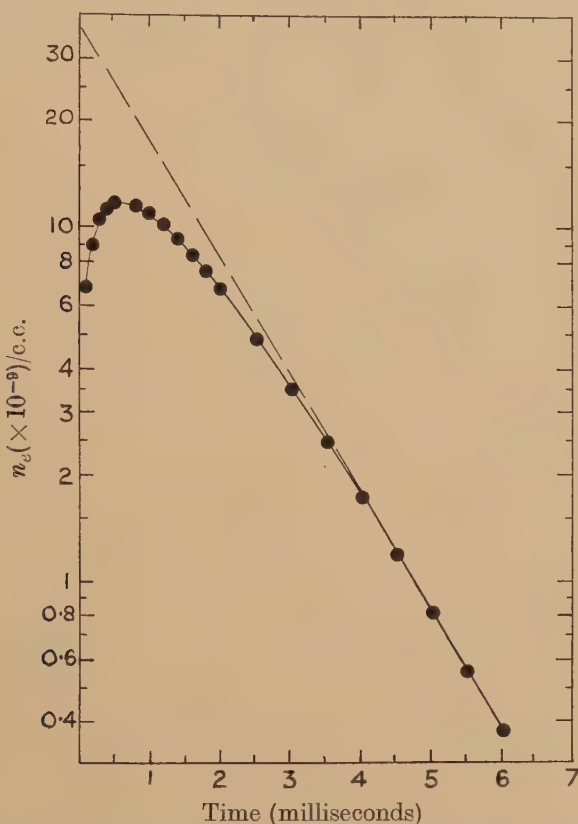
Variation of $\log n_e$ with time after cutting off a discharge in helium containing 0.1% of argon, the pressure being 7 mm Hg.

to be less than 10^{-3} times that emitted by the pure argon afterglow from which the photon yield was compatible with the observed value of α .

The mobility of the ions present in the helium-argon afterglow was determined from the data illustrated in fig. 5 as 22.4 cm/sec per volt/cm at 291° K, which is very close to that expected for A^+ ions in helium by interpolation of the data obtained by Munson and Tyndall (1939) for the mobility of the alkali metal ions in that gas.

This remarkable investigation shows quite definitely that, when molecular ions are present in only a small proportional concentration, the recombination coefficient is much reduced. It does not even follow that the radiation emitted in the mixed afterglow, which is 1000 times weaker than for pure argon, is due to radiative recombination as it may well be that the fractional concentration of ions in the molecular form is as high as 10^{-3} .

Fig. 6



Variation of $\log n_e$ with time soon after cutting off a discharge in helium containing 0.1% of argon.

Biondi (1951 b) was even able to measure the cross sections for process (23). It was found in some of the earlier microwave experiments on pure helium and neon that the electron density actually increases for about 10^{-3} sec after the field exciting the discharge is cut off. This effect is also present when the helium contains 0.1% argon. It was suggested by Holstein that this rather unexpected effect is due to ionization in collisions between metastable atoms:—



Assuming this interpretation the situation may be analysed as follows.

Once the exciting field is cut off metastable atoms are lost by diffusion to the walls, by deactivation in collisions with normal atoms, and by ionization through the process (24). Hence if n_m is the concentration of metastable atoms

$$\frac{dn_m}{dt} = D_m \nabla^2 n_m - \nu_d n_m - \nu_i n_m, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where D_m is the diffusion coefficient of metastable helium atoms in helium, ν_d is the frequency of deactivation and ν_i of ionization by (24). Under the same conditions as assumed in the discussion of §3.1 we find that

$$n_m = n_m^0 \exp(-t/t_m),$$

where

$$t_m = (\pi^2 D_m / R^2) + \nu_d + \nu_i.$$

Electrons are lost by ambipolar diffusion to the walls and produced by the process (24) so that

$$\frac{dn_e}{dt} = D_a \nabla^2 n_e + \nu_i n_m.$$

This gives

$$n_e = a \exp(-t/t_D) + b \exp(-t/t_m),$$

where

$$t_D = n^2 D_A / R^2,$$

D_A being the ambipolar diffusion coefficient of electrons and ions in the helium-argon mixture.

Both t_D and t_m may be obtained from the measured variation of n_e with t . Thus for large t the second term is negligible and the slope of the $\log n_e - t$ plot for such values of t gives t_D . Extrapolation of this linear plot to small t gives the contribution from the first term so any residual is due to the second term. This residual is found to be well represented by an exponentially varying term from which t_m may be determined. In pure helium $\nu_i = 0$ so that similar experiments in the pure gas (Biondi 1951 c) give $(\pi^2 D_A / R^2) + \nu_d$. Hence by combining results obtained with and without argon present ν_i may be obtained. In this way the cross section Q_i for the process (23) is found to be

$$Q_i = 9.3 \pm 0.8 \times 10^{-17} \text{ cm}^2.$$

It is of interest to note also that, by studying the pressure variation of the relaxation time t_m for the metastable atom concentration in pure helium, D_A which varies inversely as p and ν_i which varies as p may be separately determined. For D_A the value 520 cm²/sec was obtained. This is in reasonably good agreement with the value 370 cm²/sec calculated recently by Buckingham and Dalgarno (1952) for atoms at room temperature and with that obtained by Ebbinghaus (1930) using an optical method.

One final matter needs to be examined before everything seems to be satisfactorily cleared up. It was remarked at the beginning of this section that the mobility observed by Biondi and Brown for the positive ions in the helium afterglow at pressures below 11 mm Hg, while agreeing

with the theoretical value for He^+ ions in helium, is much less than that measured by Tyndall and Powell in their experiments on the mobility of ions from a helium glow discharge in helium. It was suggested by Meyerott (1944) that Tyndall and Powell may have actually observed the mobility of the He_2^+ ions and not He^+ at all. This suggestion has been confirmed by the recent measurements of Hornbeck and Wannier (1951) who identified both atomic and molecular ions and measured the mobilities of each by direct observation of the time taken for the ions to travel between parallel plate electrodes in a uniform field. They find 10.8 and 19 cm/sec per volt/cm for He^+ and He_2^+ ions respectively. The second value agrees quite well with Tyndall and Powell's measurements while the first is close to the theory for He^+ and to the value (13.8 cm/sec per volt/cm) observed by Biondi and Brown. At first sight it would appear paradoxical that Biondi and Brown's measurements of mobility should refer mainly to He^+ and of recombination to He_2^+ but it must be remembered that the mobility measurements are made at lower pressures which favour a larger concentration of He^+ . Support for this and for the dissociative recombination interpretation has been afforded by further studies of the variation of molecular to atomic ion concentration in the afterglow with pressure, carried out by Phelps and Brown (1952). In these experiments the positive ions diffusing to the walls of the container at different times during the afterglow were studied by a mass spectrometer. It was found that as the pressure was increased the dominant ion changed from He^+ , at the pressures of the mobility measurements, to He_2^+ at slightly higher pressures. From an analysis of the observed variation of the He_2^+ concentration with time after the discharge was cut off the rate of production of He_2^+ ions by the process



was obtained. At 1 mm pressure and 300°K the rate of formation of He_2^+ from He^+ came out to 65/sec. This is between one-half and one-third of that estimated by Bates (1950 b) from an application of the Thomson theory of three-body recombination (see §4.1). In view of the rough nature of this estimate the agreement is quite satisfactory.

There still remains the question of reconciling these results with the earlier observations (Sayers 1947) on electron decay in a helium afterglow, using Langmuir probe methods to determine the electron concentration. This discrepancy between the results obtained by the microwave and probe techniques is equally marked in observations on afterglows in argon, mercury and caesium. Although the interpretation of the data is much more difficult when more complex atoms are involved we shall briefly summarize the present position of afterglow observations in gases and vapours other than helium.

3.4. Observations on Afterglows in Other Gases

(a) *Neon.* The neon afterglow has been investigated almost as extensively as that of helium (Biondi and Brown 1949), and very similar

results have been obtained. With pure neon, recombination is dissociative, the coefficient being 2.1×10^{-7} c.c./sec. An 0.1% admixture of argon has the same effect as in helium. The mobility of both Ne_2^+ and Ne^+ has been measured (Hornbeck and Wannier 1951) and the value (4.4 cm/sec per volt/cm) found for the latter agrees quite well with that (4.1 cm/sec per volt/cm) calculated by Holstein (1950). The cross section found for the process



is about 10 times smaller than that derived by Kruithof and Druyvestyn (1937).

(b) *Argon*. Values found for α by the microwave method are 8.8×10^{-7} c.c./sec (Biondi 1951 a) and 1.1×10^{-6} c.c./sec (Redfield and Holt 1951). The second investigators found evidence of quite complex phenomena occurring. The value given was obtained with moderate power input to the microwave discharge (10 microsecond pulses and a peak power of a few hundred watts). At input powers of 1 kw peak, α falls to 0.65×10^{-6} c.c./sec.

The microwave values are much greater than those obtained by Kenty (1928) using Langmuir probe methods.

(c) *Mercury*. This afterglow has been studied by Mohler (1937 b) and Mierdel (1943) using the probe technique and by Dandurand and Holt (1951 a) and Biondi (1952) using the microwave method. In the first three investigations the electrons did not come into thermal equilibrium with the mercury atoms during the afterglow observations, but by adding some helium to the mercury Biondi was able to study the loss of thermal electrons. At pressures below 0.5 mm Hg the loss is by diffusion whereas at pressures above 1 mm Hg the loss appears to be due to attachment. Thus the rate of loss follows an exponential law with the time constants decreasing as the pressure instead of increasing as with a diffusion law. The attachment probability per collision comes out to be about 10^{-7} per collision (the attachment cross section is 7×10^{-22} cm²) which is consistent with induction attachment according to the process



At intermediate pressures the loss appears to be due to recombination with a coefficient 5×10^{-7} c.c./sec. It is of interest to notice that Dandurand and Holt find a value over 100 times smaller for electrons at a temperature of about 2000° K and Mohler an even smaller value.

(d) *Caesium*. The caesium afterglow resulting from a 10 volt d.c. discharge through caesium vapour at pressures between 8 and 300×10^{-3} mm Hg has been studied extensively by Mohler (1937 a) using optical and electrical probe methods. He found evidence supporting removal of electrons by recombination with a coefficient of between 3 and 4×10^{-10} c.c./sec. This does not agree with the microwave measurements carried out in the caesium afterglow resulting from the usual microwave excited discharge (Dandurand and Holt 1951 b).

According to them electron loss is by ambipolar diffusion at pressures less than 0.1 mm Hg. Recombination is found to be dominant above 0.3 mm Hg pressure. The coefficient found is of order 10^{-7} c.c./sec but appears to increase with the pressure. It is probable that dissociative recombination is again the important process and that the increase with pressure is due to an increase in the proportion of positive ions in the molecular form.

(e) *Hydrogen*. Richardson and Holt (1950) find that recombination predominates at pressures from about 7 to 20 mm Hg, the coefficient being about 6.2×10^{-6} c.c./sec and independent of pressure. Evidence was obtained from the simultaneous optical studies which suggests that very little radiation is associated with the recombination in this case, much of the afterglow light arising from the container walls.

(f) *Oxygen*. The decay of the oxygen afterglow under conditions similar to that of the other gases has not yet been studied in detail (see however, Biondi and Brown 1949 b) but Biondi (1951 d) had found that, at high pressures (over 8 mm Hg) and low electron densities, electron loss occurs by attachment. The attachment coefficient for thermal electrons is found to correspond to an attachment cross section of 1.2×10^{-22} cm². This is what would be expected if the process is a radiative one but the evidence from the study of attachment in O₂ by the electron filter (Bradbury 1933) and Bailey-Townsend methods (Healey and Kirkpatrick 1941) suggests a cross section about one thousand times larger. The reason for this discrepancy is far from clear at present.

(g) *Nitrogen*. A preliminary study of the nitrogen afterglow has been made by Biondi and Brown (1949 b).

3.5. Summarizing Remarks

The data obtained by the microwave method form a consistent set and are explicable generally in terms of dissociative recombination. Confidence in the method is enhanced by the agreement of the ion mobilities which it gives with those measured by other methods. It remains to clear up the big discrepancy between the microwave values and those obtained by the older methods. This may be partly due to the fact that, in the latter work, the electron density in the decaying plasma was greater. It is also probable that, in contrast to the microwave work, electrons did not come to thermal equilibrium with the gas atoms before the measurements were made. One suspects, however, that the probe techniques employed in the earlier work were not so reliable as thought at the time.

§4. RECOMBINATION BETWEEN POSITIVE AND NEGATIVE IONS

There has been no recent development in the study of ion-ion recombination comparable with that in electron-ion recombination. In view of the fact that the state of this aspect of the subject up to 1949 has been discussed by Massey and Burhop in 'Electronic and Ionic

Impact Phenomena', and of the fact that there have been no significant advances since then, we shall only give a brief review here.

Of the processes listed in §2 which can lead to recombination between electrons and ions, the radiative and three-body processes are also possible for interionic recombination. Dielectronic and dissociative recombination can no longer occur but instead there is the possibility of mutual neutralization due to charge transfer on impact between the ions:—



Radiative ionic recombination will usually be even more ineffective than between electrons and ions, so it remains to consider three-body and mutual neutralization processes.

4.1. Three-Body Ionic Recombination

As mentioned in §2.5 the theory of the three-body process has been given by Thomson (1924). Consider the interaction between two ions of masses M_1, M_2 comparable with that of a gas atom. Recombination is supposed to occur when either of two nearby ions loses so much energy in collision with a gas atom that its orbit relative to the other ion becomes a closed one. The condition that two ions when at a distance r apart should be describing a closed orbit is that the kinetic energy of relative motion be not greater than ϵ^2/r . If we take for this kinetic energy the mean value $\frac{3}{2}kT$ at temperature T it follows that the ions cannot on the average describe a closed orbit when at a distance apart greater than r_0 where

$$\frac{3}{2}kT = \epsilon^2/r_0$$

i.e.

$$r_0 = 2\epsilon^2/3kT.$$

It is now assumed that, if either ion, when within a distance r_0 from the other, collides with a gas atom to which it loses an amount of energy of order kT , recombination will occur. The recombination rate is then determined by the number s of such collisions effected by either ion when at a distance r_0 apart. Thus the recombination cross section is given by

$$Q_t = \pi r_0^2 s,$$

where $s = s^+ + s^-$, s^+ and s^- being the number of effective collisions due to each ion.

The calculation of s^+ and s^- may be carried out by elementary kinetic theory arguments. For low pressures it is found that

$$s = \frac{4}{3}r_0 \left(\frac{1}{l_1} + \frac{1}{l_2} \right),$$

where l_1 and l_2 are the mean free paths for effective collision of the respective ions in the gas. This result is valid provided l_1 and $l_2 \gg r_0$. Under these conditions the recombination coefficient is given by

$$\alpha_t = \frac{64(2\pi)^{1/2}}{81} \frac{\epsilon^6}{(kT)^{5/2}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2} \left(\frac{1}{l_1} + \frac{1}{l_2} \right).$$

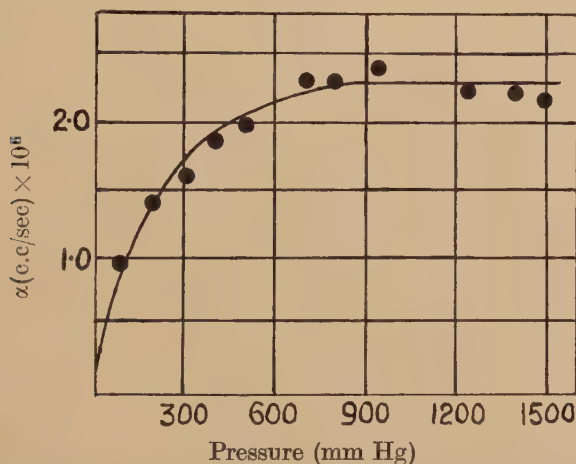
At high pressures saturation occurs, Q_t tends to $2\pi r_0^2$ and

$$\alpha_t = \frac{16(2\pi)^{1/2}}{9} \frac{\epsilon^4}{(kT)^{3/2}} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2}.$$

The theory is no longer applicable if the pressure becomes too high. In the high pressure region ($p > 1\,000$ mm Hg) Langevin's theory (1903) becomes applicable and the recombination coefficient decreases inversely as the pressure.

Experimental confirmation of Thomson's theory over a pressure range from 100–900 mm Hg in air has been provided by the work of Sayers (1938) and of Marshall, Luhr and Gardner (1938). The agreement found by Sayers is illustrated in fig. 7. The results at pressures greater than 1 000 mm Hg already indicate the departure from Thomson's theory at these pressures.

Fig. 7



Three-body recombination coefficient for ions in air as a function of pressure.

— predicted by Thomson theory.
 ● ● ● ● observed points (Sayers 1938).

Using Sayers' results and Thomson's theory the three-body recombination coefficient in air at temperature $T^\circ \text{K}$ and pressure p (< 300 mm Hg) can be written

$$\alpha_t = 8 \times 10^{-3} p / T^{5/2} \text{ c.c./sec}, \quad (28)$$

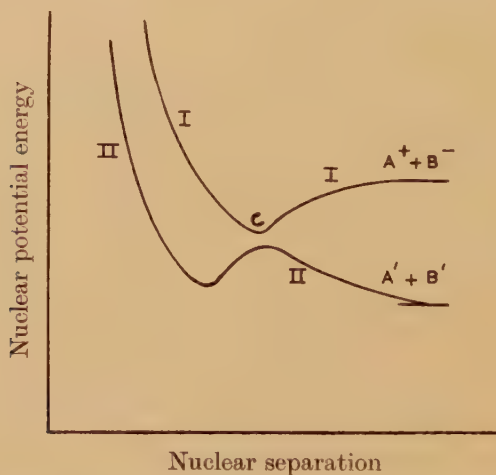
where p is in mm Hg.

4.2. Mutual Neutralization

The theory of the mutual neutralization process has been given by Bates and Massey (1943). It is best considered in relation to the crossing of molecular potential energy curves. In fig. 8 two potential energy curves are shown, for the molecule AB. Curve I leads, in the limit of large nuclear separation, to the ions A^+ and B^- and we suppose the interaction between the ions to follow this curve if they approach with

infinite slowness. At the point C , however, the curve I approaches very close to a second curve, II, which in the limit of large nuclear separation goes over to neutral atoms A' and B' in the ground or some excited states. If the ions approach with finite velocity there is a chance P that at C the state of the system will jump from curve I to curve II. The chance that on passing C the states will still lie on curve I is $1-P$. Having reached the closest distance of approach the relative motion of the systems will reverse and there is again a chance P of a transition occurring at C . The net result is that the chance of the systems emerging on the curve II is $2P(1-P)$. This will be small if P is small or nearly unity. The former case is the nearly adiabatic one of a very slow approach, the latter is the one where the interaction between the two molecular

Fig. 8



Illustrating the process of mutual neutralization.

states is very weak (in the limit of vanishing interaction the curves would actually cross at C and the identifications of the curves inside C would be interchanged). The probability P will depend on the relative angular momentum of the two systems so that the cross section for mutual neutralization can be written

$$Q_m = \sum_{l=0}^{\infty} 2P_l(1-P_l)q_m, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where q_m , the maximum partial cross section for a relative angular momentum $\{l(l+1)\}^{1/2} \hbar$, is given by $(2l+1)\pi/k^2$. k is the wave number of the relative motion, given by

$$k = (M_1 M_2 / M_1 + M_2) v / \hbar,$$

v being the relative velocity of the ions and $M_1 M_2$ their masses.

a molecule XY whose ionization potential is less than that of O (it could be O₂ or NO) recombination would proceed through the processes



If the first process is much faster than the second, the latter is rate determining and the effective recombination coefficient α will be effectively that for the dissociative process (34). Moreover, α will still be independent of the pressure. On the other hand, if the first process is rate determining most of the ions at any instant will be O⁺. If $n(\text{O}^+)$ is the concentration of these ions, $n(\text{XY})$ that the of molecules XY, we shall have

$$\frac{dn(\text{O}^+)}{dt} = q - \beta n(\text{O}^+)n(\text{XY}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where β is the rate coefficient for the process (33). Since most of the positive ions are O⁺, $n(\text{O}^+) \simeq n_e$, the electron concentration, so

$$\frac{dn_e}{dt} = q - \beta n_e n(\text{XY}). \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Comparison with (31) shows that in this case

$$\alpha = \beta n(\text{XY})/n_e.$$

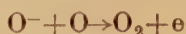
It will increase with pressure due to $n(\text{XY})$ and depend on n_e just as if the electrons disappeared by attachment to neutral molecules XY with an attachment coefficient β . This may well be the state of affairs in the F_2 layer, the extreme thickness of which suggests that the rate of electron loss in it decreases as the pressure decreases, so maintaining a high equilibrium electron concentration to very high altitudes.

It is difficult to make these considerations quantitative. It is possible to show, however, that even if the cross section for the charge transfer process (33) is no larger than 10^{-17} cm², the proportional concentration of the molecules XY need be no greater than 1/100 in order that (34) be rate determining. It is not impossible that O₂ or NO molecules are present in such proportions in the F_1 layer.

Apart from the main layers, there is also an ionized region below the E layer, known as the D region, which extends down to some 70 km. Normally this ionization does not have any marked influence on radio propagation but at times of solar flare activity the ionization is considerably enhanced and causes radio fadeouts. The strong absorption of the radio waves under these conditions is due to the high collision frequency of electrons at these lower altitudes. There is little information about the value of the effective recombination coefficient in this region. One might expect that the negative ion electron ratio λ would be sufficiently large for mutual neutralization to make an important contribution through the term $\lambda\alpha_i$ in (32). However, if the observations of the nature and rate of electron loss in oxygen are correct

(see §3.4 (f)) it is probable that, even in the *D* layer, negative ions are not present in sufficient quantity to contribute to the effective recombination of electrons in the daytime.

All the above considerations apply only to recombination during the day when photodetachment is very effective in reducing the negative ion concentration. In the *F* layer the pressure is so low that there is no time for any important concentration of negative ions to build up during the night but this may not apply to the *E* layer and below. As we have insufficient knowledge of the rate of detachment at night due to such processes as



it is not possible at present to discuss the night-time effects in any detail.

§ 6. RADIATIVE RECOMBINATION PHENOMENA IN ASTROPHYSICS

Radiative recombination plays an important part in many astronomical phenomena. It would be out of place in this review to attempt to describe all these phenomena in detail, but we shall indicate briefly one example of such an application of recombination theory, the theory of the solar corona.

There is now no doubt that the kinetic temperature of this extreme outer region of the sun's atmosphere is very high, about 10^6°C . The most definite evidence for this is the identification by Edlén (1942) of the coronal emission lines as due to transitions between states of the ground configuration of Fe XIV. The presence of iron atoms in such a high degree of ionization would hardly be possible if electrons of high energy were not present to maintain the ionization rate. Apart from this there is a variety of indirect evidence which leads to the same conclusion. It is important for many purposes to know something about the quality and quantity of the radiation emitted from the corona. For example, if the intensity of the coronal radiation in the high frequency region is far in excess of that expected from the usual model of the sun as a black-body at $6\,000^\circ\text{K}$, its influence in the production of ionization in the terrestrial atmosphere might be profound (Hoyle and Bates 1948). A start has been made by Woolley and Allen (1948) towards the theoretical investigation of coronal emission.

As the kinetic temperature in the corona is very much higher than the radiation temperature it is impossible to use statistical arguments in this problem. Woolley and Allen show first that the ionization equilibrium can be regarded as arising from a balance between ionization due to electron impact and radiative recombination. Thus, consider the equilibrium between the *s*th and (*s*+1)th stages of ionization of a particular atom. If there are *nx* atoms/c.c. ionized in the (*s*+1)th stage and *n*(1-*x*)/c.c. in the *s*th, the number of atoms entering the (*s*+1)th stage per c.c. per second due to ionization by electron impact will be

$$n(1-x)n_e\gamma \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where *n_e* is the electron concentration and *γ* is the ionization coefficient given by the mean value of *vQ_i(v)*, *v* being the electron velocity and *Q_i*

the cross section for removal, by impact of an electron of velocity v , of a further electron from an atom already in the s th stage of ionization. The contribution from photoionization is negligible.

The number leaving the $(s+1)$ th stage per c.c./sec. due to radiative recombination with electrons is

$$n_x n_e \alpha, \quad \dots \dots \dots (38)$$

where α is the radiative recombination coefficient. Hence, in equilibrium,

$$n_x n_e \alpha = n(1-x)n_e \gamma,$$

giving

$$\frac{x}{1-x} = \frac{\gamma}{\alpha}. \quad \dots \dots \dots (39)$$

Woolley and Allen estimated γ by analogy with available data on ionization cross sections and α from the data of table 1 assuming it to be proportional to S^2 where S is the charge on the ion. In both cases the kinetic temperature was taken as 10^6 °C. In this way they found that x approaches unity when the energy required to further ionize an atom already in the s th stage of ionization is about 400 ev. This is in agreement with the spectroscopic evidence, showing that the assumption of the high kinetic temperature is consistent. Having shown this, Woolley and Allen proceed to discuss the abundance of different elements in the corona and thence the nature of the normal emission. For details of this work the original paper should be consulted.

A further astronomical application of radiative recombination theory is to the study of the chemical composition of interstellar gas (Strömgen 1948, Bates and Massey 1941, Seaton 1951). This work depends again on a study of the equilibrium between atoms of an element in different stages of ionization. Under the conditions of interstellar space the important process tending to the degree of ionization is not electron impact but photoionization. The relation (39) is then replaced by

$$\frac{x}{1-x} = \frac{\Gamma n_e}{\alpha}$$

where Γ is the coefficient for photoionization of the atom from the s th to the $(s+1)$ th stage and α is the radiative recombination coefficient. The details of the work will be found in the papers referred to.

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Surface Effects in Plastic Deformation of Metals

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SUMMARY

It is now accepted that the appearance of slip bands on the surface of a plastically deformed metal is evidence that the deformation is not homogeneous but is concentrated on relatively few atomic planes. Recent microscopical experiments have suggested that this conclusion is only valid in the later stages of deformation and that the first fractional per cent of strain is much more nearly homogeneous. Theories to account for both these stages of deformation are examined in the light of microscopical evidence.

The validity of conclusions about internal processes based on experiments on the surface is discussed; it is shown that the surface finish affects not only the appearance of internal processes but also the processes themselves.

In cases where the deformation is not homogeneous the balance of evidence is that it is also not continuous in time: instead, slip on an active slip plane tends to a limit which is reached either gradually or suddenly depending on the nature of the metal and the conditions of stress. The same processes which stop slip on the active planes produce general hardening of the metal. However, slip can restart on or near to former slip planes as a result of mechanisms activated by temperature and stress, and can, in favourable cases, continue until fracture. Therefore slip bands, the sources of hardening, are also places of weakness.

§ 1. INTRODUCTION

1.1. *The Inhomogeneity of Plastic Deformation*

It was first shown by Ewing and Rosenhain (1900), and by Rosenhain (1905) that the dark bands seen on the surface of a plastically deformed metal crystal were really steps formed, as it appeared, by shearing slabs of atoms over each other along well-defined slip planes, much like cards in a pack. The thickness of each slab as measured by the spacing of the steps is of the order of a few microns for most metals. The distance each slips over its neighbours can be calculated from the macroscopic shear strain and is of the order of a few thousand atomic diameters. There is apparently no relative movement of the atomic planes within a slab. Thus it can be concluded that slip in metals is inhomogeneous and is all concentrated on a few widely spaced atomic planes. The knowledge that the deformation is inhomogeneous however, has until recently, only rarely been applied in the study of deformation of metals. Most such studies employ the methods of engineering, that is the measurement of macroscopic quantities such as the stress-strain relationship for a large specimen.

At the other extreme the theoreticians have had some success in explaining the phenomena of the yield stress and of work hardening, by using the concept of dislocations, which are crystalline imperfections on an atomic scale. On an intermediate scale, there has been a great deal of study by means of x-rays of the lattice strains produced by plastic working. Until recently, this work involved averaging strains over dimensions of the crystals large compared with the width of the slabs.

It is surprising that inhomogeneity of strain should have been taken for granted to such an extent. If it is assumed that a single crystal first yields to an applied stress on some particularly weak slip plane, then it is necessary to account for the fact that slip does not continue on this plane until fracture occurs but shifts to others. The usual explanation is that it is due to work hardening: slip does not occur by simple sliding of slabs of atoms over smooth planes leaving the crystalline lattice undamaged apart from a translation of some parts. Instead the lattice around the active slip plane is supposed to be severely distorted, so that a higher stress is required to make slip continue on the original plane. Deformation can, however, continue on one of the still perfect atomic planes. This hypothesis fails to account for some observed facts about slip bands. The first is that slip occurs by visible amounts on each, that is over distances of 1 000 atoms or so. It does not seem reasonable that so much movement should be possible before the current slip plane becomes harder than some other plane still undamaged. Secondly, it has long been known, certainly since the work of Yamaguchi (1928), that slip bands once formed can increase in shear at the same time as new bands are formed. If work hardening is due to damage to the active slip planes, one would expect that the planes on which slip has never occurred, being more perfect, should be planes of easier slip than those which have slipped already.

1.2. *The Stress-Strain Curve*

The stress-strain curve is the macroscopic expression of the microscopic processes going on in the crystal. Mathematical expressions can be fitted to the curve and it is even possible to create the illusion of an equation of state for plastic deformation. But the processes of slip, being on a scale accessible to the microscope, can be studied by themselves. It should not be necessary to describe them by means of purely statistical equations. Similarly a study of the mechanics of individual dislocations moving in the stress field of other dislocations does not, of itself, provide a satisfactory explanation of the slip bands, which involve the apparently simultaneous movement of some hundreds of dislocations.

An illustration of the effect of purely statistical reasoning on the study of metallic deformation is provided by the situation still existing in the study of creep, that is of strain as a function of time at constant stress. Here it was shown by Andrade (1914) that there was a definite equation for the relation between strain and time and that the form of this relation was applicable to many different polycrystalline metals. It has been

since shown that the same relation applies with only minor modification to the creep of many substances, metallic and non-metallic, crystalline and amorphous under all sorts of conditions of stress and temperature. Now it is obvious that the mechanism of plastic flow in these materials must differ, but the mathematical equation holds for all because it is basically a statistical relation and is based on an average view of the processes going on in the whole crystal. It is probable that the very universality of the Andrade relation has discouraged the study of creep by means of the microscope. It is only very recently that serious attempts have been made to find if creep strains are also inhomogeneous (McLean 1952, Trotter 1952).

In the case of the stress-strain curve many attempts have been made to fit it to an equation of state for plastic deformation. If these had been more successful it is possible that the study of plastic deformation as a function of stress would have been today in as primitive a state as the study of creep.

§ 2. MICROSCOPICAL EVIDENCE ON DEFORMATION OF CRYSTALS

2.1. *Study of Slip by the Electron Microscope*

Interest in the problem of why slip occurs by large amounts in narrow bands was stimulated when Heidenreich and Shockley (1947) examined the slip bands on aluminium single crystals by means of the electron microscope. They found that the slip bands visible in the light microscope can be resolved into clusters of finer lines. This was interpreted as meaning that the steps found by Ewing and Rosenhain were not sheer steps formed by slip on one plane, but were terraces of smaller steps formed by slip over several parallel slip planes spaced some 100 atoms apart. These slip planes can thus be looked on as the boundaries of elementary slip lamellae and it was found that each of these lamellae had slipped over its neighbours a distance of about 2 000 Å. The experiments of Heidenreich and Shockley have now been repeated in many parts of the world (Brown 1949, Nishimura 1951, Yakutovitch 1951), and general agreement is obtained at least as regards what is seen. There is however, some disagreement about the interpretation of the micrographs. For reasons which will appear below this work has not been extended to many other metals; but, for such as have been covered, similar results are obtained (§ 2.6).

It is essential to view results obtained with the electron microscope with the greatest caution. Firstly, it is well known that metals cannot be examined directly in the electron microscope. Instead a replica of the surface relief has to be prepared thin enough to transmit electrons: in one method a plastic solution is caused to flow over the surface and when the solvent has evaporated the resulting film, which is usually a few hundred ångströms thick, is stripped off and used as an object in the electron microscope. It is obvious that a spurious structure can be introduced in

such a thin film during the stripping process. In particular, plastic films shrink by unpredictable amounts when freed, and results which involve measurement of electron micrographs from replicas are therefore seldom accurate. The resolving power of a plastic replica is limited by the size of the molecular aggregates in the plastic and is much inferior to the resolving power of the electron microscope itself. Some reliable authors quote a figure for the smallest structure which can be resolved as large as 400 Å.

In the case of aluminium however, a replica of much greater resolving power is provided by the metal's own oxide film. This is built up electrolytically to a thickness of perhaps 200 Å and it can then be easily stripped off undamaged, by chemical attack on the aluminium surface, though only at the cost of destroying the specimen. The resolving power of such a replica is about 50 Å and the interpretation of the resulting micrographs is less ambiguous than by any other method.

In the study of deformation of metals by means of the electron microscope it has been found that the main difficulty is in relating the results directly with light microscopy. The fidelity of the replicas themselves is no longer in doubt. Recent work by Hyam and Nutting (1952) has shown by means of optical and electron micrographs from the same areas of various specimens that, at least as far as the resolution of the light microscope allows, the replicas are extremely faithful. In studies of deformation the magnitudes involved are usually much less than the resolution of the light microscope and it would be desirable to be able to compare each electron micrograph with the corresponding optical micrograph. However, the field of the electron microscope is small; of the order of a few microns. The number of slip bands which can be seen is correspondingly small, seldom as many as ten. The methods employed are at best chancy and, in the case of aluminium on which most of the work has been done, involve the destruction of the specimen. Thus it is not possible to observe stages in the deformation of the same specimen nor is it in general feasible to select the desired parts with the light microscope for examination with the electron microscope. For this reason the tendency has been to compare the few results obtained with the electron microscope with results observed optically on other specimens and with results quoted in the literature. While this is not very satisfactory it does not seem possible to improve on it, in the present state of electron microscope technique, without a prodigious amount of work. It would be necessary to repeat, by means of combined electron and light microscope methods, the results in this field of the past 50 years.

2.2. *Study of Slip with the Light Microscope*

The stimulus of these results of the electron microscope has led, however, to an intensive search of the literature for data on slip bands. A particularly comprehensive review of past work has recently been made by Kuhlmann (1950). The main conclusion to be drawn from her review is that there is

considerable disagreement between observations of the same phenomenon by different authors. The majority of the results have been descriptive rather than involving measurement, and where measurement has been attempted the results have not been reproducible. The reason for this state of affairs is now beginning to be understood: slip bands are a manifestation on the surface of mechanisms within the crystal; the crystal itself is far from being the simple almost perfect three-dimensional array of atoms which the early workers assumed; the mechanisms producing large amounts of slip on relatively few slip planes are complex and easily disturbed by small changes in the crystal structure and in the conditions of test. Finally, it has recently been pointed out (§ 3.2) that slip processes occurring under identical conditions in one crystal may appear quite different on patches of the surface which have been prepared in different ways. It will be convenient to summarize the points where general agreement in observation is obtained, mentioning how recent work may clear up such discrepancies as remain. Matters where there is still little or no agreement will be left till later.

Firstly, it is generally agreed that slip bands on all metals increase in number during deformation. At the same time, the amount of shear in each visible band usually increases. The relative rates of these two processes differ for different metals and also with differing temperatures of deformation and conditions of strain and strain rate. In some cases one of the two processes may occur too infrequently to be observed; for example, Andrade and Hutchings (1935) and Andrade and Roscoe (1937) have shown that in some of the hexagonal metals slip bands may, as the strain increases, grow in depth but seldom in number. Some of the views contrary to this can now be accounted for by confusion between the slip bands which grow in depth and their constituent lamellae which, as will be seen later (§ 2.4), do not.

The only other subject on which there is agreement, is the effect on the slip bands of changing the temperature of deformation: the higher the temperature, the further apart are the bands spaced and the greater is the shear on each. Thus for example in a pure aluminium single crystal deformed to a shear strain of say 10% at liquid air temperature, the slip bands are fine lines spaced about 2 microns apart. The same deformation at room temperature produces slip bands which, even in the light microscope, are markedly broader and are perhaps 6 microns apart; while if the deformation takes place at 200° C the bands appear to be very broad and about 20 microns apart.

2.3. Interpretation of the Fine Structure of Slip Bands

Brown (1949) has attempted to interpret these observations on the basis of the fine structure discovered by Heidenreich and Shockley (1947). He finds that the lamellae which make up the slip bands do not alter appreciably with strain, with temperature of deformation or with rate of deformation. The only major difference is in their grouping into bands.

At very small values of the strain, slip occurs by amounts of approximately 2 000 Å on planes separated by distances of the order of tens of microns. As the deformation increases new slip planes become active and slip by the same amounts. The effect of temperature is that the higher the temperature the greater is the tendency for these new slip planes to be very close to old slip planes. Figures 1-6 (Plate X) show how the groups of slip planes at various temperatures appear in the electron microscope. In the light microscope each group of closely spaced slip planes appears as a single dark band. At very low temperatures the new slip planes are usually located about midway between the old ones giving the appearance in the light microscope of fine closely spaced bands (figs. 1-2, Plate X).

Small differences are discovered between the slip distance per active slip plane at different temperatures. Mean values are given by Brown (1950 a) are

Temperature °C	Average Slip Distance (ångström)
-180	1600
20	2000
250	2200

It is doubtful whether the values found for 20°C and 250°C are significantly different, but it does appear that at liquid air temperature the distance the elementary slip lamellae can slip relative to each other is a little less than at high temperatures. This result is confirmed by a very few experiments which have been carried out on the deformation of aluminium at the temperature of liquid helium (Brown 1952). It appears that there is a real shortening of the slip distance as the temperature is reduced towards absolute zero. In support of this, Yamaguchi and Togino (1929) found, by averaging the macroscopic strain over all observed slip bands, that the average slip distance was about 25% less at liquid air temperature than at room temperature. Further confirmation comes from the experiments of Holden (1948), described in § 2.5.

2.4. *Jerky Deformation*

The significance of the averages given above is dependent on the assumption that slip on an active slip plane takes place at all once, that the slip distance is not built up over a period of time, and that once the slip plane has acted it does not readily slip again. Brown (1950) claims that all these assumptions are justified as far as the accuracy of observations with the electron microscope will allow.

The evidence for this claim is the regularity of the elementary slip steps observed on many specimens. Steps involving slip of half the unit, or less, are not found (except under the special conditions of surface, referred to later). Neither are steps found with much more than the quoted slip distance. Such conclusions, if correct, are important for the theory of the formation of slip bands, so it is appropriate to review here such additional evidence as is available.

The first definite evidence that slip takes place on a slip plane by a definite amount in a very short space of time was provided by A. A. Joffe (1928 a) who with Miss M. W. Klassen found that the shear of heated rock salt and zinc ' progresses by small jumps each accompanied by a noise like the tick of a clock '. The magnitude of the individual jumps was found to be constant at a given temperature but was reduced as the temperature of deformation was reduced. More recently, Maddin, Mathewson and Hibbard (1948 and 1949) observed that the slip lines on α -brass reached a fixed depth in an immeasurably short space of time. It will be shown later that it is reasonable to identify the slip lines seen on brass by these workers with the elementary slip lines seen on aluminium as the constituents of slip bands.

A further proof that slip on an active slip plane is by a fixed amount is provided by some other electron microscope studies. Here Brown (1951) found that in aluminium single crystals deformed at a temperature of 450° C at a constant strain rate of 1% per day the elementary slip lamellae all corresponded to a slip distance which did not vary markedly from the usual 2 000 Å in spite of the fact that the deformation took place over a time of the order of a fortnight. Figure 13 (Plate XII) is a low magnification photograph of the slip bands formed in this experiment. Each of these bands consisted of some 50 lamellae a few of which are shown in the electron micrograph in fig. 14 (Plate XII). If slip could occur for a second time on a once active slip plane it would have done so under these conditions, for which considerable recovery of work hardening would be expected.

Finally, in the experiments of Cahn (1951) on cross-slip it was found that when slip jumped from one active slip plane to another parallel one by means of slip on a third intersecting slip plane, lamellae tended to make the crossing individually, separated by distances which could be resolved with the light microscope. This phenomenon is shown in fig. 10 (Plate XI). A macroscopic view of cross-slip is shown in fig. 9 (Plate XI). Now, a theory of cross-slip described by Mott (1951) and due to Frank, shows that while slip on the slip plane of maximum shear stress occurs in a narrowly defined region, there is no reason why this should be so for cross-slip, the position for which is determined by more accidental factors. Thus, on the planes of cross-slip a slip line need not be observed ; instead there may be a fuzzy broad mark. However, it is found that the lamellae usually cross over apparently intact (fig. 10, Plate XI), suggesting that each elementary slip process takes place as a unit, presumably in a short space of time.

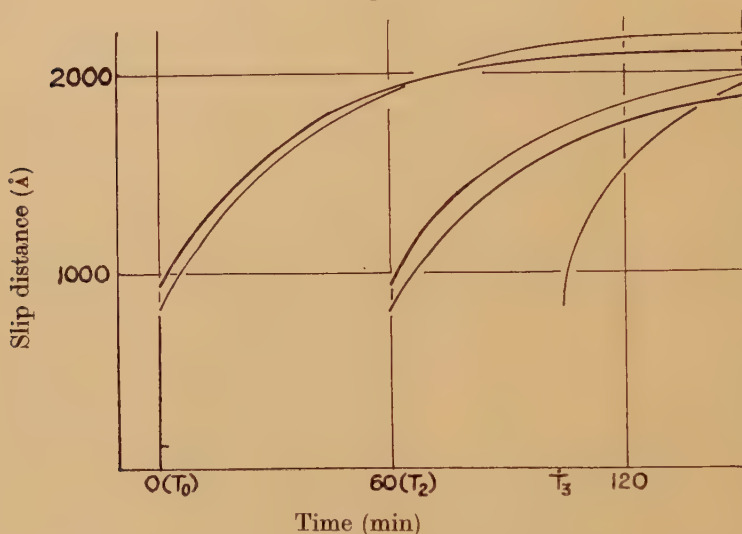
2.5. *Measurement of the Slip Distance by Interferometry*

Tolansky and Holden (1949) have used Tolansky's (1948) method of multiple beam interferometry to study the heights of slip steps. By this means, step height and hence slip distances can be measured with an accuracy of perhaps 100 Å by displacement of interference fringes. A typical view of the surface of an aluminium single crystal deformed to a

shear strain of about 0.5% is shown in fig. 11 (Plate XII). The sloping lines are interference fringes, each is faulted as it crosses the slip steps (vertical traces) and the amount of faulting is a measure of the step height.

The uniformity of the heights of the steps due to the various slip bands is striking: the average height is about half the interfringe distance, that is one-quarter of the wavelength or about 1 300 Å. From this, knowing the crystallographic orientation of the specimen it can be calculated that the slip distance in the slip plane and slip direction is about 2 000 Å. At such a strain each slip band consists of only one elementary slip process and thus the value obtained for the slip distance is in agreement with that determined by electron microscopic means.

Fig. 15



Growth of Slip Bands in Slow Strain (after Holden (1948)).

When the loading is carried out at rates such as are used in tensile testing, the steps are found to appear suddenly and not to increase much with increasing load. The range of values for the slip distance at strains corresponding to the expected appearance of one elementary slip step per band was 1 400 to 2 200 Å.

In experiments at slow strain rates Holden (1948) was able to study the growth of each slip step. The progress of a typical experiment is shown in fig. 15. A shear stress of 0.81 kg/mm² was applied to an aluminium single crystal at time T_0 ; two slip bands appeared in the field of view and the slip distance corresponding to each were measured at intervals until T_2 by which time the bands had apparently ceased to grow. The stress was then increased to 0.92 kg/mm² activating two more slip bands in the field of view. Finally at T_3 the stress was increased to 1.09 kg/mm² adding a fifth band to those being measured. In spite of the low strain

rate the curve shows that the bands all appear suddenly with a slip distance of about 1 000 Å. In this experiment the limiting slip distance as determined from 10 slip bands was exactly 2 000 Å, all measured values being in the range 1 800–2 200 Å.

In a parallel experiment with a specimen immersed in liquid air it was not possible to measure the step heights continuously, but the mean limiting slip distance for 10 bands was 1 750 Å, all values being between 1 550 Å and 1 900 Å.

In these experiments the step height corresponds to only one slip process of 2 000 Å per band and to a band spacing of over 40 microns. While the resolution of the multiple beam interferometer in the direction parallel to the surface is sufficient to allow experiments to continue to band spacing of the order of 5 microns, its effectiveness as a measure of surface topography is lost as a result of surface rumpling. Figure 12 (Plate XII), however, shows interference fringes on the surface of a specimen deformed about 1%. It can be seen that some of the step heights correspond to a full fringe (2 700 Å) and thus to a slip distance of about 4 000 Å, while most of the others are only half this value.

Figures 11 and 12 show further that slip does not take place by pure translation of slabs of atoms over each other in the manner stated in the introduction. For if it did, the interference fringes would acquire a stepped appearance such as is shown in fig. 16 (b) instead of the sawtooth appearance shown in the photographs and diagrammatically in fig. 16 (c). (In figs. 16 (a), (b) and (c) the interference fringes have been drawn, for clarity, normal to the slip bands; in figs. 11 and 12 they are at an angle of about 45°.) Instead the zones between slip bands are rotated through a small angle about an axis parallel to the slip planes and perpendicular to the specimen axis. The reason for the rotation appears to be constraint at the grips. The curvature of the lattice in the region between slip steps obviously shows the presence of an excess of dislocations of one sign trapped on each slip plane.

2.6. *Experiments on Metals other than Aluminium*

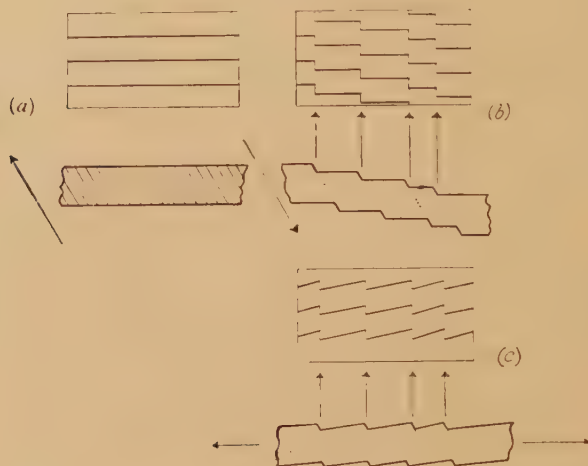
For reasons given in § 2.1 most of the electron microscope studies of slip bands have been done with aluminium. Now, in aluminium the spacing of the elementary slip lines which make up the clusters is from 200–800 Å. Thus, no matter how carefully the light microscope is used it cannot resolve them except in a few cases, such as in cross slip, when their separation is increased. Even in these cases however, resolution is still difficult since, when using the light microscope for highest resolution, the depth of focus may be insufficient to allow more than two steps of height 1 000 Å to be in focus together.

For this reason there is, in aluminium, a clear distinction between slip bands and elementary slip lines: the former are spaced at distances greater than the resolution limit of the light microscope and the latter are not. If it were not clearly observable that the bands grow in size with

increasing strain and the elementary slip lines do not, the distinction would appear to be an artificial one depending on the resolution of a microscope, that is on the wavelength of an illumination.

In some metals such a distinction cannot be made. For example, Straumanis (1932) found that in single crystals of zinc continuous improvement in the resolving power of his light microscope resulted in the appearance of more and more slip lines at finer and finer spacings. There was no obvious grouping into bands. Recent work with the electron microscope on cadmium has shown a similar state of affairs: examination of the surface

Fig. 16



Study of slip by multiple beam interferometry (after Holden (1948)).

- (a) Interference fringes and crystal before deformation (slip planes shaded).
 (b) Interference fringes and crystal after deformation by simple translation on slip planes. (c) Interference fringes and crystal after deformation in tension.

of a deformed cadmium single crystal by means of a new replica technique of high resolving power due to Brown (1952) has revealed slip lines at spacings down to about 600 \AA (fig. 17, Plate XIII). These lines represent steps the height of which varies from a few hundred angströms to a few thousand. What is significant is that they appear to cover the entire crystal, and there is nothing which could obviously correspond to the slip-free inter-band region in aluminium and other cubic metals. Now it is well known that when a cadmium single crystal is deformed it develops widely spaced bands which can often be resolved by the naked eye. With the aid of a lens the appearance of widely spaced bands is

lost and the surface seems to be covered with fine lines. With the electron microscope the number of lines is again found to increase and the appearance of the crystal is as stated above. Since in the electron micrograph the minimum spacing is much greater than the resolving power of the electron microscope and the replica process, it seems reasonable to conclude that the lines seen are the ultimate slip structure and that nothing finer would be seen at dimensions of larger order than that of atoms. It further seems reasonable to conclude that the ultimate slip lines are constituents of slip bands and that the spacing of the former is such as to give maxima and minima of density which result in the impression of bands visible to the naked eye. However the field of view of the electron microscope is too small to confirm this. Again, in the few cases when cross-slip has been observed in cadmium (figs. 18 and 19, Plate XIII) it seems that definite units of slip cross from one slip plane to another in a manner similar to that observed in aluminium.

The experiments of Maddin, Mathewson and Hibbard (1948 and 1949) on slip and cross slip in α -brass revealed a fine structure extremely like that found on aluminium except that in brass it could be resolved by the light microscope (figs. 7 and 8, Plate XI). The authors found that fine lines were, in general, grouped in what they called macro-lines (fig. 8). The spacing of the fine lines was upwards of 1000 Å, but was much less regular than in aluminium: in particular, slip lines of apparently the elementary size were found in positions isolated from the macrolines. The slip distance on each elementary line was about 5000 Å, but was again not so regular as in aluminium. There are indications that the fine slip lines on brass, although irregular and resolvable by the light microscope, are indeed elementary slip lines, the boundaries of elementary slip lamellae and the constituents of slip bands exactly as found in aluminium. Firstly, they cannot be further resolved by the electron microscope using a replica technique with a resolving power of 200–300 Å. Secondly, Maddin, Mathewson and Hibbard were able to show that their so-called macrolines or clusters of fine lines grew as deformation proceeded by the addition of more fine lines. The number of clusters increased only slightly with increasing strain and the fine lines themselves did not grow after their first appearance. Thirdly, cross-slip in α -brass takes place by the transference of fine slip lines intact from one slip plane to another, exactly as in aluminium and, apparently, cadmium. Figure 7 (Plate XI) shows prominent cross-slip, that is, cross-slip between slip clusters. Figure 8 (Plate XI) shows intimate cross-slip, that is, slip between the slip lines comprising one cluster.

Figures 20 and 21 (Plate XIV) show the resolution of slip bands on a single crystal of tin. The experiments, which will be described later (§ 8.5), were made to compare slip bands in polycrystalline specimens with those in single crystals, and not enough were done to establish a regularity in the fine structure.

For other metals the results are much less satisfactory. Fine structure has, according to Seitz (1952), been detected in slip bands of copper by Craig and Czyzewski. Figures 26 and 27 (Plate XV) are electron micrographs of slip on a copper single crystal: the bands are not resolved. Measurement of the faulting of one system of bands by the other, with due allowance for the component of slip normal to the surface, gives a value for the slip distance of 1 500 Å for the smaller black band in fig. 26 and 3 000 Å for the larger.

2.7. *Crystals apparently without Fine Structure in their Slip Bands*

It is clear from the preceding paragraphs that it is too early to say if there is fine structure in the slip bands of all metals. However, judging by the established facts for aluminium and brass, the important fact is not the existence of a resolvable fine structure, but rather the observation that slip takes place by more or less definite amounts on each active slip plane. It is therefore a pity that one of the best demonstrations of this—the jerky deformation effect described in § 2.4—has been observed only with zinc and rock salt. In neither of these crystals has fine structure been definitely shown to occur in their slip bands. In the case of zinc the lines Straumanis found at the limit of resolution of the optical microscope were very regular, but it has not yet been shown if they were indeed the ultimate structure. In the case of rock salt considerable effort has been made to resolve a fine structure in the slip bands but without success.

In § 7 of this paper suggestions will be made as to why some of these elementary slip processes should cluster in slip bands while others form the nuclei of new bands. None of these processes require that the spacing of the clustered slip processes should be resolvable; some would work equally well for successive elementary slip processes on the same slip plane.

If this attitude is adopted to the significance of fine structure, the irregularities in the apparent elementary slip distance in cadmium and copper could be explained as being due to successive elementary slip processes on unresolvably close slip planes.

2.8. *Sideways Growth of Slip Bands*

It is frequently observed that slip bands do not, on their first appearance, run right across the crystal surface, but extend sideways as deformation proceeds. Thus, in the interior of the crystal there is a region which has slipped, imbedded in a surrounding region which has not. The slipped zone spreads with increasing stress until it either covers the whole crystal itself or combines with another slip process on a neighbouring slip surface. This growth of a region of slip is consistent with the idea of slip spreading from a source (§ 5.2).

Since sideways growth takes place much more slowly than growth in the direction of the applied stress, and since it produces a more striking effect on the surface, it lends itself more easily to study. The experiment

of observing the sideways growth of slip bands by means of cinematography was first done by Yamaguchi (1929) and has recently been repeated by Chen (1952). Neither of these authors, however, has taken account of the effect of differences in the manner of preparation of the surface. It is observed that, on specimens polished purely electrolytically, it is much rarer to find a slip band which neither runs right across the crystal nor runs into another one. Now in § 3.3 it is suggested that a slip process approaching a surface can more easily break out if the surface has been distorted by mechanical polishing. Thus, in the specimen prepared by electropolishing only it is more likely that the slip process will be held up under the surface and will thus be able to spread over a larger fraction of the cross-sectional area before it appears as a visible slip band.

In electron micrographs ends of slip bands are rather rare objects. A few which have been observed show that the surface step does not die away gradually near the end but ceases quite abruptly: the distance from a point where the step has its full height to a point where it is not visible is only a micron or so.

This is in agreement with the view (§ 7.4) that slip appears on the surface only when sufficient dislocations have collected under the surface.

§ 3. IS THE SURFACE OF A METAL TYPICAL OF CONDITIONS IN THE INTERIOR ?

3.1. *Slip Processes within the Metal*

The relevant evidence as to the nature of slip provided by the microscope has been summarized above. Now the microscope can only observe the surface, while theories of slip must take account of processes within the bulk of the metal. Before discussing these theories and such further microscopical evidence as is available on them, it is necessary to investigate just how far the appearance of the surface is typical of conditions within the metal.

3.2. *The Effect of Surface Preparation on the Appearance of Slip Bands*

The assumption that plastic deformation is inhomogeneous is based almost entirely on experiments on the surface. Doubt as to the reliability of surface studies of deformation has recently arisen as a result of the discovery by Brown and Honeycombe (1951) that it was only if the metal surface was rubbed with abrasive before electropolishing that the usual coarse widely-spaced slip bands appeared after small deformation. On parts of the surface which had not been abraded, but had been polished purely electrolytically, they found none of the usual type of slip bands but only diffuse markings parallel to the bands in the abraded zones. The apparent spacing of the diffuse markings varied with the position of the microscope objective, and they were not visible at all with the electron microscope. These facts are consistent with the suggestion that the diffuse

markings are bulges on the surface rather than steps. As deformation proceeded, the coarse slip markings in the abraded zones increased in number as well as in height. What happened to the diffuse markings could not be properly determined, but the general appearance of the surface remained unchanged except that there also appeared among the diffuse bands some sharper lines parallel to them. These latter markings were shown by the electron microscope to resemble slip bands but to have slip distances as small as 200 Å (fig. 25, Plate XV). At still higher deformations the appearance of the abraded and unabraded zones became identical except that in the unabraded zone the slip bands had always the background of diffuse markings. If the crystal was then repolished so as to remove all traces of slip, the bands appearing on both zones after further deformation were of the usual coarse type.

3.3. *Micro-slip*

Figure 23 (Plate XV) shows the appearance of the boundary between the abraded and unabraded regions on an aluminium single crystal deformed 5% in tension. On the left (abraded region) the slip bands are well defined, while on the right (unabraded region) there are a few well-defined slip bands together with many more ill-defined markings parallel to them. Figures 24 and 25 are electron micrographs from the abraded and unabraded regions respectively of another aluminium crystal. The replica method used shows up the slip bands as black bands running diagonally from top left to bottom right. In fig. 24 the slip distance is about 5 000 Å per band: in fig. 25 it is, in some cases, less than 200 Å. The small slip bands have been called micro-slip. The furrow-like structure running almost vertically across figs. 24 and 25 is explained in § 6.3.

Figures 26 and 27 are from the abraded and unabraded regions of a copper single crystal extended 5%. Here slip (black) is shown faulting a scratch (white). In fig. 26 (abraded zone) there are only two slip bands, the slip distances of which are respectively about 1 500 Å and 3 000 Å. In fig. 27 (unabraded zone), as well as the 3 000 Å fault, there are many finer markings parallel to it crossing the scratch. These may be interpreted to be micro-slip similar to what is observed in aluminium.

On the conventional view that slip takes place in the interior of a crystal by large amounts on widely separated planes, these experiments show that an undistorted surface is a barrier preventing these slip processes from leaving the crystal. It is only if the perfection of the surface is destroyed either by local surface working or by general working of the whole crystal that large slip steps can appear. The nature of the surface obstruction could be an oxide film if it were not that the effect has also been observed on deeply etched unpolished surfaces of aluminium (§ 5.9) as well as on gold, where an oxide film is very unlikely. Alternatively it could be argued that more energy is required to break a perfect surface (and allow the slip processes to leave) than to break one which has been distorted by cold work.

Another view is that the fine slip bands which are always observed on specimens free from previous mechanical distortion are an indication that slip, in the early stages of deformation, takes place by small amounts on many slip planes. This quasi-homogeneous deformation ceases immediately as a result of surface work or gradually as a result of general working of the whole specimen. The mechanisms proposed to account for micro-slip will be considered along with the mechanisms of ordinary slip in § 5. Meantime it is sufficient to stress that micro-slip is a small effect, only producing an appreciable fraction of the total shear during the first few percent of deformation. However, it presents a case when the surface has been shown to be an unreliable guide to what is happening in the interior.

3.4. Methods of Investigating Appearance of Slip in the Interior of a Crystal

It is extremely difficult to devise an experiment to decide whether the abraded surface or the unabraded surface reveals the true state of affairs in the interior. There are various experiments which show that in the interior most of the strain is by large amounts on isolated planes. There are, for example, the experiments on transparent crystals first performed by Obreimov and Shubnikov (1927) and recently improved by Nye (1949). In these a crystal of rock salt or silver chloride is examined between crossed nicols. It is found that when the crystal is extended the field of view becomes crossed with narrow bright bands corresponding in position with the slip bands on the surface. This proves that there are coarse slip bands which run right through the crystal. It does not show if there are also fine slip bands between them, and it is unlikely that the method could be made sensitive enough to detect the small strains which are suspected on many relatively closely spaced planes, since the spacing of the micro-slip planes is expected to be of the order of 100–1000 Å, much less than the resolving power of the birefringence method.

Again, there are the experiments which show that under certain conditions slip planes can be etched. It was observed by Jacquet (1945), McLean (1947) and Burke and Barrett (1948) that markings were obtained by special etchants on the surface of deformed crystals from which the slip bands had been erased by polishing. They were able to show that these markings were traces of slip bands which were thus concluded to run right through the specimen. Doubt as to the validity of some of these experiments was expressed by Hibbard (1948), who found that, at least at small strains, successful etching of slip bands was dependent on the surface steps not being fully removed by polishing. The usual electropolishing techniques were sufficient to remove the slip traces as seen in vertical illumination, but there was still a small surface curvature left which could be made visible by oblique illumination. The curvature resulted in preferential etching of the former slip bands. Even if polishing techniques are used which completely erase the steps,

it is clear that the method could not pick up the closely-spaced micro-slip. If, however, a specimen with abraded and unabraded regions were examined by this technique in the strain range where only diffuse markings are seen on the unabraded regions, it might be possible to show that the former regions showed no strain markings on polishing and etching, while the latter did. It would be necessary to improve the technique in order to be sure of etching up the relatively fine slip bands corresponding to such a small strain in the abraded regions.

The experiments of Blewitt and Koehler (1950) on slip in ordered alloys seem to give some hope of a definite answer. They reasoned that if an ordered alloy is sheared then, if slabs of metal move relative to their neighbours by an odd number of atoms, the effect would be to disorder the alloy and produce a large increase in resistivity. Measurement of the increase for a macroscopic specimen would then show whether the movement had been on a few planes or on many planes. They found results "not in disagreement with Heidenreich and Shockley", who found that at first the deformation is on isolated planes. If deformation had been on many planes, even by small amounts, then about half of these micro-slip planes would have moved by odd numbers of atoms and a larger increase in the resistivity would have been measured. This seems conclusive, but it will be shown when the mechanisms of micro-slip are considered (§ 5.8) that it is possible that the effect of micro-slip might not be noticed in resistivity measurements.

Some experiments by Paxton, Adams and Massalski (1952) suggest another way of deciding the matter. These authors have shown that if patterns are marked out by scratching the surface of an electropolished iron crystal and then the scratches polished off, the patterns return after deformation in the form of patterns of coarse slip amid a field of diffuse markings. This is in agreement with Brown and Honeycombe. Paxton, Adams and Massalski have, however, shown further that slip is continuous from micro-slip to coarse slip: each coarse slip band degenerates into a bundle of fine slip bands at the edge of the scratch. A test on these lines with a series of closely spaced parallel scratches might be conclusive, for if the coarse slip is fundamental to the interior then it should be possible to follow a coarse slip band across several scratches. Such a band will simply split into a more or less parallel bundle of fine slip as it passes into each region between the scratches, re-uniting at the next scratch. If, on the other hand, the micro-slip is the true state of affairs in the interior, then there is no reason why it should unite to form coarse slip in the same way in two successive scratches, and it will not be possible to follow coarse slip bands across the specimen. A picture published by these authors suggests that the latter is the case but, since slip bands in iron are notoriously erratic, a more careful study is needed. An obstacle however to the application of this method is that, as has been shown by various authors and as will be mentioned later, the surface is not just a passive observer of the events inside the metal. The surface

can also influence these events. In particular it will be shown (§ 7.7) that scratches influence slip-band production in their neighbourhood. For this reason it is doubtful if observations of the distortion of reference scratches will decide for or against homogeneous slip. A suggestion by Seitz (1952) that the reference marks might be slip bands of another system is hopeful, but only if the cold work accompanying the appearance of reference bands can be annealed out without destroying the surface finish. Repolishing would, of course, destroy the reference marks.

To sum up: there is no definite evidence as yet as to whether the first few thousandths of deformation may be quasi-homogeneous slip, but such evidence as is available suggests that it is. If so, the evidence of the electropolished surface is correct. However, there is no doubt that at higher deformations slip is inhomogeneous, as has been hitherto assumed, and the evidence of either the mechanically polished, or the electropolished, surface is correct.

Once having decided the nature of microslip it is not difficult to devise experiments to investigate its magnitude and distribution. Thus Kurnosov, Tronina and Yakutovitch (1948) showed by means of a micro-interference method that in the early stages of deformation of a zinc crystal the visible slip bands could not account for more than a small fraction of the macroscopic strain. Holden's experiments, referred to in § 2.5, gave no indication of slip other than in the slip bands, but the surface was of necessity ground optically flat before electropolishing. If it were subsequently annealed and re-electropolished its profile as revealed by multiple beam interferometry would give some guide to the amount of strain not included in visible slip bands.

§ 4. THEORIES OF THE SPACING OF SLIP BANDS

4.1. *Microscopic Contributions to Theories of Slip*

Few, if any, of the advances in the understanding of metallic deformation have been the result of microscopy. For example, the concept of dislocations was due to attempts to explain the low value of the yield stress and the facts of work hardening, and the geometry of slip was worked out by x-ray crystallographers. Thus it is inappropriate to review here more than those fragments of the theory which have either resulted from microscopical observations or which can be tested by microscopical observations.

4.2. *Regularity of Slip Bands*

Superficial observation of the slip bands on a deformed metal leaves two impressions on the observer. Firstly, the spacing of the bands seems regular, and secondly, all the bands look alike. The former has come to be almost a dogma of metal physics; several attempts have been made, notably by Orowan (1941) and Bragg (1942), to explain the regularity, but few to test it by statistical means. Many authors have measured the average spacing of slip bands and drawn conclusions therefrom without

considering how the spacings are distributed about the mean. Thus Yamaguchi (1928), Cox and Clenshaw (1935), Crussard (1945), Rosi and Mathewson (1950) and many others have related the average spacing of the slip bands and the yield stress. Andrade and Hutchings (1935) and Andrade and Roscoe (1937) measured the slip-band spacing for cadmium, lead and mercury at various strains and found that the mean spacing was almost independent of strain. Indeed, in lead the mean spacing was independent of temperature and rate of deformation as well.

The reason for the regularity of slip-band spacing has recently been discussed by Orowan (1951). He rejects the idea that the spacing is predetermined in the virgin crystal by the existence of regularly spaced planes of easy slip. Since the slip-band spacing is regular at all strains this would require that the softest planes were distributed at one spacing throughout the lattice, then the next softest planes were distributed at another spacing, slightly closer than for the softest planes, and so on.

On the other hand, Andrade and Roscoe (1937) concluded from their experiments on lead that the slip bands were predetermined by accident of growth in those metals where they were found to be laid down at the beginning of deformation and did not increase in number as the deformation went on. In the case of metals which behave in this way, Orowan's argument does not dispose of the possibility of predetermined slip planes. Another possible explanation of the non-increase in the number of slip bands is that the neighbourhood of a once active slip plane is really a soft part of the metal. This is considered later (§ 7).

In the harder metals then, at least, it seems agreed that the slip-band spacing is determined by interaction of the bands one with another. Large numbers of dislocations become accumulated on slip planes (§ 4.6), and these dislocations produce stresses in the lattice which make it difficult for slip to occur within a zone on either side of the slip plane. A difficulty of this theory is that the range of the stresses due to dislocations in a plane array is much too small to explain even the closer slip band spacings observed, let alone those at the start of deformation (see however Mott 1952).

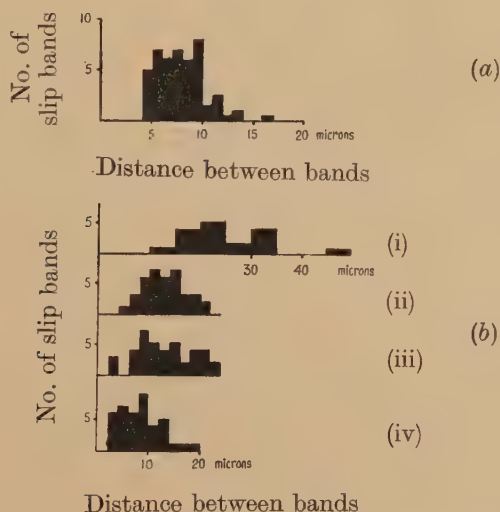
4.3. *Distribution of Slip Band Spacings*

In some recent experiments, attempts have been made to produce a histogram of the spacings. Typical results are reproduced in fig. 28. The number of observations in these, as in other attempts, is not large enough for much accuracy to be claimed, but the consistent result is obtained that the histogram corresponds to an apparently random distribution of the larger spacings, but deviates from the random at small spacings. The curve cuts off at a minimum spacing which depends on the macroscopic strain, being at smaller spacings for larger strains. The number of observations of spacings shorter than the apparent cut-off which would be required to make the observed histogram indistinguishable from the random curve is very small; only about three in fig. 28 (a). However, the consistent absence of these short spacings suggests that

there is a minimum spacing for slip bands and that this minimum depends on strain. The existence of such a minimum can only be explained by the interaction of adjacent bands: there is on each slip band a lattice disturbance which inhibits slip in a more-or-less definite region on each side. The average spacing seems to be about twice the cut-off value.

Barrett (1944) plotted similar histograms for slip band spacing on specimens of copper and monel. The spacings in this case were determined by the electron microscope. It was found that apparently all spacings for about 0.3μ to 2.5μ were equally probable in copper. None were found below 0.3μ , although the method would have resolved

Fig. 28



Histograms of Slip Band Spacings on Aluminium Single Crystals.

- (a) Aluminium single crystal extended 7% at room temperature. Mean slip spacing on the surface 8μ .
- (b) Changes in the distribution of slip band spacings with increasing deformation. Slip band spacings at four stages of deformation of an aluminium single crystal (each histogram is based on the same total number of slip bands).
- (i) Extension 0.7%. Mean spacing 25μ .
 - (ii) Extension 2.5%. Mean spacing 12μ .
 - (iii) After repolishing and further extension to 3.8%. Mean spacing 13μ .
 - (iv) After repolishing again and further extension to 7%. Mean spacing 9μ .

spacings of a tenth of this value. In the case of monel, however, the histogram showed a very marked peak at 0.3μ and spacings down to the resolution limit were also found. It might be concluded from these results that 0.3μ corresponded to the most common lamellar spacing for monel and that most of the slip markings so spaced were really constituents of slip clusters. A similar histogram for aluminium, not

distinguishing between slip bands and slip lines, would show a marked peak at about 200 Å. Apparently the resolution of Barrett's method was insufficient to resolve the slip bands in copper.

4.4. *Theories of Work Hardening*

It is to be concluded from the above that the cause of slip band separation is the stresses set up by a concentration of dislocations on the slipped planes. These stresses make it more difficult to force a slip process through the metal. The macroscopic yield stress thus rises with increasing density of slip bands and the metal is said to work harden. Thus the prime cause of work hardening, whatever may be its detailed mechanism, is disorder on the slipped planes.

4.5. *Trapping of Dislocations on Slip Planes*

The experiments mentioned in § 2.4 showed that slipped planes were themselves very hard, in the sense that a very high stress would be needed to force another slip process across them. Even after long periods at 450° c planes which have once slipped do not soften sufficiently to slip again. It can hence be concluded that a high density of dislocations is left behind when a slip process crosses a slip plane. There is other microscopical evidence for the existence of these trapped dislocations: it is well known, for example, that the appearance of slip band fields on the opposite faces of a flat single crystal of the cubic metals is seldom even approximately the same. This means that some of the slip processes have not run right across the crystal and thus that dislocations are trapped in the interior. There is the evidence produced by Cahn (1949) that dislocations have been produced during plastic deformation, have not been able to leave the crystal and are available to form dislocation arrays known as polygon boundaries.

Again the x-ray studies of Warren and Averbach (1949 and 1950) showed that there was disorder in cold worked metals involving lattice strains of rapidly varying sign. Estimates of the spacing of dislocation lines in a cold-worked metal vary, but an apparently reliable estimate is that of Koehler (1941) which is that in the state of highest work hardening of a metal about one atom in 30 is on a dislocation line.

4.6. *Location and Distribution of Trapped Dislocations*

While the above results show that there are large numbers of dislocations trapped in a cold-worked metal, they give no indication of how these dislocations are distributed—whether singly or in groups—or where they are situated. Certain microscopical evidence, however, suggests that the trapped dislocations are located on the slip planes. Firstly, Nye (1950) has shown from his study of transparent crystals that slip 'planes' are curved, thus indicating that there was an excess of dislocations of one region distributed along the slip planes. The same result was obtained for metallic crystals by Holden (§ 2.5). Again Castaing and Guinier (1949) have shown that age hardening precipitates

from preferentially on formerly active slip planes in the same way as they form on polygon boundaries (figs. 29 and 30, Plate XVI). Polygon boundaries are certainly rows of dislocations, so it is reasonable to suppose that the same is true of slip bands.

As to distribution of the dislocations on the slip planes, it will be shown in § 4.7 that it is reasonable to suppose they are not evenly distributed at, say, one every 30 atoms, but are collected in clumps.

The dislocation density calculated by Koehler is only reached throughout the metal after intensive cold rolling; but in view of the result obtained above regarding the hardness of slipped planes it can perhaps be concluded that a spacing of this order is reached on every slip plane after a slip process has passed over it.

4.7. *The Interaction of Slip Bands*

If the distortion due to a slip process running across a crystal is limited to the immediate neighbourhood of the slip plane, it is difficult to see how slip planes can interact with each other to give hardening: the formula usually quoted for the stress τ at distance r from a dislocation is due to Koehler (1941) and is

$$\tau = \frac{G}{2\pi} \frac{1}{1-\nu} \frac{a}{r},$$

where G is the elastic shear modulus, a is the atomic spacing and ν is Poisson's ratio.

If the dislocation considered is one on a slipped plane, it is easy to see from this formula that no substantial movement of dislocations can take place within a distance from the slipped plane d given by

$$d \sim \frac{1}{2\pi} \frac{G}{\tau_a} \cdot \frac{a}{(1-\nu)},$$

where τ_a is the applied shear stress. Now G/τ_a is of the order of 1 000, so that d is about 200 atoms. This formula thus could explain the spacing of the fine structure in aluminium but not of the slip bands under any conditions. Even at the highest strains at liquid air temperature the spacing of slip bands in aluminium is at least 1 000 atoms. In particular this explanation of the slip band spacing cannot account for the fact that the spacing is regular even at the smallest strains and remains so throughout deformation.

The formula above, however, gives the result that the number of slip bands per unit distance is proportional to the stress, a result which has been obtained experimentally for aluminium by Yamaguchi (1928) and also by Cox and Clenshaw (1935). Kuhlmann (1950) has also calculated the same result using some experimental observations on silver by Gough and Cox (1931).

4.8. *Dislocation Clumps*

Better agreement between theory and practice could perhaps be obtained if, instead of a row of dislocations spaced closely along the

slip plane, there were a series of clumps, rather as suggested by Cahn (1949), as the model for polygon boundaries. The stress due to a clump of n dislocations would be of the order of n times the stress given by the Koehler formula. Thus the clumps would have to contain some hundred dislocations to give reasonable agreement with observed slip band spacings. In this connection, it is interesting to note that in the experiments of Castaing and Guinier referred to above (§ 4.6) the precipitates on the slip bands were not arranged continuously along the bands but were about 1 000 Å apart. If the density of dislocations is really one every 30 atoms, or a dozen per 1 000 Å, the presence of the precipitates suggests that the dislocations may indeed occur in small clumps on the slip bands. The same 1 000 Å separation was found for precipitates on polygon boundaries, again in agreement with the idea of clumped dislocations (figs. 29 and 30, Plate XVI).

The considerations above suggest that it is necessary to fill the space between slip bands with something more substantial than elastic stresses. In fact, it seems impossible to avoid the conclusion that there are dislocations left, not only on the nominal slip planes but also in the inter-band regions. Possible sources of such dislocations will be considered later.

§ 5. THEORIES OF THE ORIGIN OF SLIP BANDS

5.1. *The Need for Dislocation Production Mechanisms*

The most remarkable feature of slip is the concentration of the deformation into slip bands separated by regions where slip is not detected. From light microscopy it was known that in deformation of the cubic metals at room temperature the slip distance per band was of the order of $\frac{1}{2} \mu$ at ordinary strains. The width of the slip band was less than the resolution limit. Thus it was not known how slip was distributed in the band, how many slip planes took part and what was the profile of the slip step formed. For example, deformation might have been homogeneous within the limits of the band with a slip distance of about 10 atoms per slip plane. Electron micrographs, as usually interpreted, show that in aluminium the band profile is a series of steps. Each step represents slip of about 700 atoms and the observed sharpness of the step shows that this slip is concentrated onto less than ten neighbouring atomic planes. Some recent experiments by Yakutovitch and others (1951) which suggest that deformation on each step is really a zone of concentrated homogeneous deformation on about 50 neighbouring planes will be described in § 5.9. The following account is based on the presently accepted view.

If it is assumed that a slip step on the surface is produced when dislocations, travelling along the slip plane, leave the crystal, it is thus necessary to account for a number between 70 and 700 dislocations on every atomic plane in the lattice. This number alone is greater than can be assumed to exist in the virgin crystal, but added to these it is

necessary to account for the presence of the dislocations left on the slip plane after deformation and which thus have not left the surface. If the figure of one dislocation every 30 atoms is accepted, then the number required on each slip plane of a crystal of reasonable size runs to many thousands.

5.2. Frank-Read Sources

It is therefore necessary to have multiplication mechanisms by which the few dislocations present in the annealed crystal can produce many thousands of others. Many attempts have been made to devise such a mechanism; the most favoured at present is that due to Frank and Read (1950), whereby apparently unlimited amounts of slip can take place in a slip plane by the rotation of a dislocation round an anchor provided by a dislocation in another plane.

While it was the evidence of the microscope which raised the need for dislocation multiplication mechanisms, it is difficult to obtain direct evidence by which the mechanism proposed can be tested. In the case of Frank-Read sources the idea for the multiplication mechanism is based on the spiral growth in crystals, for which there ample evidence has accumulated and has recently been summarized by Frank (1952) himself.

Fig. 31



Sterile slip.

5.3. Sterile Slip

Since the Frank-Read sources operate in the interior of the metal they can be observed only by their effect on the surface, that is by the slip bands. A test of this theory would thus be to see if slip bands which became isolated from their sources ceased to grow with increasing deformation. Such an interpretation can be put upon the behaviour of some slip bands:

It is found, particularly at high temperatures, that in regions where cross slip is common some branches of slip bands appear much narrower than corresponds to the strain (fig. 9, Plate XI). The reason for this has been observed by the author and Dr. Honeycombe, during observations of the growth of slip bands with increasing strain. It has not yet been possible to obtain a satisfactory set of photographs of the growth of non-uniform slip branches. Figure 31 shows schematically what is seen. With increasing deformation the slip band in fig. 31 (a) develops a branch (fig. 31 (b)). This branch is really a new slip band which has run into the former one. As deformation proceeds slip continues on the kinked band but not on the lower branch which goes sterile (fig. 31 (c)). If now the

surface is repolished to remove all slip bands and then re-strained, the kinked slip band reappears. The sterile branch does not (fig. 31 (*d*)). The inference to be drawn from these observations is that there was a Frank-Read source on the left-hand portion of the slip band in fig. 31 (*a*). This joined up with the source feeding the new band to produce the kinked band. The right-hand half of the original band, being divorced from its supply of dislocations, went sterile.

5.4. *Frequency of Frank-Read Sources*

If the above interpretation of fig. 31 is correct and slip bands can indeed go sterile for want of a Frank-Read source which can be activated, it seems to show that Frank-Read sources are relatively rare occurrences within the crystal. This is in agreement with Orowan's views which will be described in § 5.5. It is not in agreement with Mott (1951) who concludes that there should be about 10^{12} sources per cubic centimetre of metal.

Since growth in a slip band in aluminium is by the formation of lamellae, there is another conclusion to be drawn from these observations: all lamellae in a band come from the same source or group of sources working together. For if this were not so, suppose the lamellae to be formed by independent sources which have been able to operate because they happen to be close to existing slip planes. Suppose further that the original source dies after producing enough dislocations to make one elementary line. Then, under these conditions, the sterile branch is as likely to slip as the other branches.

Other evidence for the bands being due each to one source is given by the experiments at high temperatures and slow strains described in § 2.4. Figure 14 (Plate XII) shows cross-slip within a gross slip band, which may contain 50 lamellae. Cross-slip involving whole bands is also observed and in such cases all 50 or so lamellae wheel round in unison on to the cross-slip plane and back to the original plane. Since the band is formed one lamellar slip at a time it may be assumed that the cross slip arose during the establishment of the first lamellae, through the uniting of two Frank-Read sources on adjacent planes. If now two new Frank-Read sources are required to form every kinked lamellae, it is inconceivable that all should produce the macro-cross slip in even approximately the same place.

Cottrell (1952), in arguing that all lamellae arise from one Frank-Read source, considers that this implies that all slip on a band is fundamentally on one slip plane and that the resolvable lamellae only arise as a result of obstacles to slip. This will be discussed later amongst evidence on the origin of lamellar slip (§ 7).

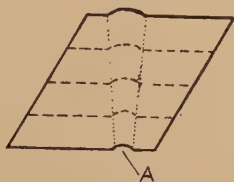
5.5. *Dynamic Multiplication Mechanisms*

Orowan (1951) has criticized the theory of Frank-Read sources as it is usually presented, on the grounds that there is no provision for slip to spread to other slip planes, there being no provision for the creation

of more Frank-Read sources on parallel slip planes. Such a mechanism is necessary since, on Orowan's reasoning, it is impossible that there could be a Frank-Read source on every plane which can be an active slip plane at some stage of the deformation. Even if it is accepted that each lamellar slip does not require a separate source this argument is not invalidated since it has been shown (§ 4.2) that the sites for slip bands are selected by factors other than the availability of 'soft' planes.

Other arguments developed by Orowan for the existence of a dislocation mechanism whereby slip may be propagated on parallel slip planes are the existence of kinking and of the punch effect. In kinking large numbers of parallel slip planes act apparently simultaneously. The slip may be confined to the small length of each plane within the kink band, and, though the amount of slip of each may be so small that slip markings cannot be observed microscopically, it cannot be reasonably assumed that a sufficient number of dislocations pre-existed on all the active slip planes.

Fig. 32



The punch effect (after Orowan).

In the punch effect first observed by Jillson (1950) a zinc single crystal cleaved along its basal planes (fig. 32) is struck by a hemispherical punch at the point A. It is found that the indentation runs right through the crystal and appears on the opposite face undistorted in shape but somewhat larger in size. Orowan concludes that this is again a case of kinking: in particular, within the boundaries of the punch channel slip must have occurred almost simultaneously on many slip planes. There must thus exist a multiplication mechanism which can propagate slip not only in its own plane but also in parallel planes.

It is outside the scope of this article to describe Orowan's mechanism in detail. Briefly, however, he maintains that if the velocity of a moving dislocation can approach a critical velocity which is about half that of sound the plane of maximum shear stress in front of it is no longer the slip plane but is a plane inclined to it. At the limiting velocity the plane of maximum shear stress is at 45° to the slip plane. Thus a slip process moving across a slip plane sprays out dislocations on either side of it. These 'side-steps' can then act as Frank-Read sources.

5.6. Microscopical Evidence for Dynamic Multiplication Mechanisms

Leibfried (1950) claims that, because of thermal damping, moving dislocations cannot reach the velocities, sufficiently close to the velocity

of sound for dynamic multiplication mechanisms to work. This has, however, been queried by Nabarro (1951), and it is interesting to look for experimental evidence of dynamic multiplication mechanisms. Such evidence might include :—

- (1) Evidence that slip processes can leave the slip plane.
- (2) Evidence of dislocations in the regions between slip bands.
- (3) Evidence of the effect on slip bands of conditions under which dislocations cannot reach the necessary high velocities.

These will be considered in order.

(1) A dislocation leaving the slip plane will continue only until its energy is dissipated. It must then either return to the direction of maximum shear stress and continue parallel to its original direction, or stop. In the former case it is seen by the microscope as intimate cross-slip; that is cross-slip of lamellae within a slip band. The usually accepted view of macro-cross-slip, described by Mott (1951) in which cross-slip is produced by the near approach of slip processes in adjacent slip bands, each with its own Frank-Read source, is not applicable here since it is unlikely that each fragment of an elementary slip line could possess an activatable Frank-Read source. The other case, when the moving dislocations stop, applies to those which are sprayed out beyond the limit of the band. They may be visible as incompleated short slip lines on either side. Figures 33 and 34 (Plate XVII) show an effect frequently observed, especially on specimens deformed at high temperature: the slip band is surrounded by a structure like feathers.

(2) The presence of dislocations in the interband region is shown by the incompleated slip processes described above. Again, it has been shown in § 4 that if all dislocations left behind by the slip process are concentrated on slip bands, it is difficult to account for the band spacing.

The evidence of the microscope is thus indirect. Seitz (1950), however, in a discussion of the x-ray work of Warren and Averbach mentioned in § 4.5, concludes that if the dislocation density in cold worked aluminium is as high as in α -brass, then many dislocations will be situated in the regions between visible glide elements.

(3) The conditions under which dislocations are unable to reach high velocities were reviewed by Brown (1952). His paper pre-dates the theory of Frank-Read sources and summarizes the experimental evidence for the then current theories that slip bands were the result of avalanches of slip. It was supposed that one dislocation, set in motion by the applied stress approached the speed of sound and gained enough energy to produce more dislocations. These were in turn accelerated and produced more until a whole avalanche of slip was moving across the slip plane. The avalanche was eventually stopped by work-hardening on the slip plane.

It is now believed that slip bands are not necessarily the result of fast dislocations but can be produced by slow-moving dislocations by the mechanism of Frank and Read. If however, we accept Orowan's conclusion that a multiplication mechanism for Frank-Read sources

is required, and that such a mechanism requires fast dislocations, the evidence of Brown's paper is still valid. If there are no fast dislocations there will be no multiplication mechanism, not enough Frank-Read sources and few, if any, slip bands. The following account is modified on these lines.

5.7. 'Slipless Flow'

Any cause which prevents dislocations from reaching high velocities can prevent multiplication mechanisms from operating and so inhibit slip-band production. There are the following possibilities:—

- (a) The temperature of deformation may be too low. The speed of sound is then higher. However, since thermal damping is less the change in slip distance resulting from temperature change is not likely to be large.
- (b) Foreign atoms in solution may hinder dislocation movements.
- (c) Precipitates may hinder dislocation movements.
- (d) The rate of strain may be too low to induce high velocities of slip.
- (e) The grain size may be so small that the accelerating dislocation reaches a grain boundary before it attains the critical velocity.

These will be considered in turn.

(a) It is found that in aluminium the elementary slip distance falls with falling temperature of deformation from 2 200 Å at 250° C to about 1 000 Å at the temperature of liquid helium (§ 2.3). For a given strain the density of slip bands is actually increased by reducing the temperature of deformation.

(b) The effect on slip bands of impurities in solution has not been carefully studied. It is however known that in specimens of commercial aluminium the elementary slip processes are only slightly shorter than in aluminium of purity 99.995%. Moreover, specimens of aluminium containing magnesium, copper, or zinc in solution up to the limit of solubility always show slip bands.

(c) The effect of precipitates has been studied by Smith and Dewhirst (1949) in their work on internal oxidation. They allowed oxygen to diffuse into a flat polycrystal of copper containing 0.6% of aluminium in such a way that in the zones immediately under the surface the aluminium was transformed into precipitates of alumina about 1 000 Å in diameter. When such a metallic sandwich was bent, ordinary slip bands were observed in the non-oxidized region, but these bands stopped at the boundaries of the oxidized region. Slip bands were not observable in the oxidized region either by light microscopy or by electron microscopy (figs. 35 and 36, Plate XVIII).

Similar results have been published by Edeleanu (1952), who has found that slip bands which are present in a solution-treated alloy of 93% aluminium and 7% magnesium are absent under identical conditions in the aged alloy, in which there are precipitates of a second phase (figs. 37 and 38, Plate XVIII). In specimens where ageing is not complete, a few slip bands are still found (fig. 39, Plate XVIII).

In Smith and Dewhirst's experiments the specimens were mechanically polished; in Edeleanu's they were polished purely electrolytically. In neither case were diffuse markings noticed instead of slip bands. Thus the deformation in the supposedly slip-free zone may have been truly homogeneous.

It has apparently never been reported whether or not slip bands are observed in age-hardened dural. However, the nature of the precipitates in the aluminium-4% copper alloy is quite different from that in either of the above two alloys. In the latter the precipitates were large and roughly spherical, while in dural, Castaing and Guinier (1949), as well as Buinov and Lerinman (1950), have shown that the precipitates, if there are any, are thin flat plates.

(d) and (e) In sufficiently slow creep the rate of acceleration of the dislocations may be low, and the distance they have to travel to reach the critical velocity correspondingly long. If, then, the grain size in a creep specimen is small, slip bands may be absent. This effect was first noted by Hanson and Wheeler (1931) and has recently been carefully studied by Wood and his collaborators (1950), who find that at a given temperature the missing slip bands can be made to reappear either by increasing the strain rate or by increasing the grain size. Again, at higher temperatures a larger grain size is required to suppress slip. Figure 13 (Plate XII) shows that in large single crystals slip bands appear at quite high temperatures and very slow strain rate.

At first sight these results support the theory of Leibfreid that the actual speed of dislocations is limited by scattering by heat waves and is thus less at higher temperatures. However, experiments with single crystals suggest that slip bands disappear from the grain of a polycrystalline aggregate when the grain size is less than the distance between slip bands on a similarly deformed single crystal. It is not known how slip bands would behave under conditions when there is not room for two in the same grain.

The effect of grain size also affected Edeleanu's experiments. It was found, for example, that in an aged specimen of widely varying grain size slip bands were absent in the smaller grains and present in the larger grains. Since the precipitates should not have been affected by grain size, the effect must be due to the differing free paths of the dislocations in the different grains.

The effect of very high rates of deformation is considered in § 9.

5.8. *The Origin of Micro-Slip*

The evidence previously presented on the diffuse bands observed on electropolished specimens gives some support to the conclusion that slip in the early stages of deformation is on many more planes than was previously thought. Brown and Honeycombe (1951) reason that most of these planes soon cease to function because "dislocations on planes as closely spaced as the micro-slip interact strongly, preventing further

movement except of a relatively small number of slip planes". They add: "This mechanism can also account for the high rate of strain hardening in the early stages of deformation when the coarse bands which are usually observed are too far apart to interact." This argument is unsatisfactory as it requires dislocations to be created in large numbers on the closely-spaced slip planes. Such creation requires the operation of Frank-Read sources. Apart from the difficulty of creating or activating so many sources during deformation by less than 1%, there seems no reason why they should stop acting at a shear so far below what they usually produce.

A more interesting possibility is that the micro-slip is due to dislocations already in the virgin lattice. These diffuse without multiplication to the edges but do not leave the surface to form steps. By this means the observation that the diffuse slip appears in the form of surface bulges is explained. The rapid rise in the strain hardening is explained by the fact that the lattice is impoverished in dislocations. Since the loss of dislocations will not affect the electrical conductivity much the smallness of the fall in conductivity found in the experiments with ordered alloys (§ 3.4) need not be taken to mean that only a few slip planes are active. In fact, deformation by such an exhaustion process may increase the conductivity slightly and still further reduce the effect of the true slip processes.

A test of this theory would be to see if, in a carefully handled electro-polished crystal, the first fraction of 1% of plastic strain and strain hardening can be recovered by reversing the stress.

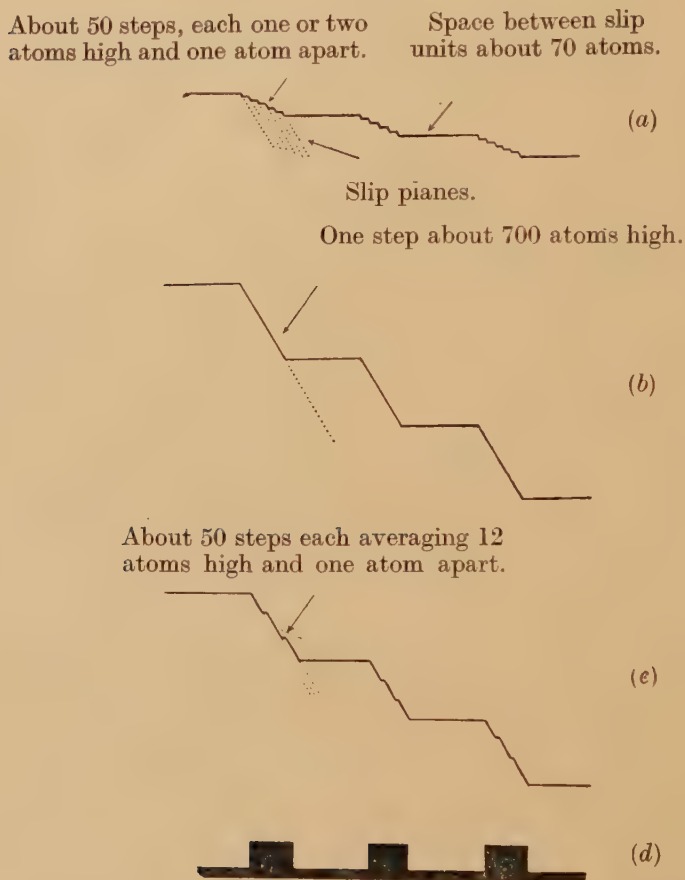
5.9. *A Compromise between Homogeneous and Inhomogeneous Slip*

Reference has already been made (§§ 2.1, 5.1) to the work of Yakutovitch, Yakovleva, Lerinman and Buinov (1951), who have repeated the experiments of Heidenreich and Shockley (1947). Since the more recent paper is not yet well known, the main points will be summarized before discussing their implications:

Single crystals of 99.95% aluminium were deeply etched in aqua regia to produce the usual cubic block structure. The surface was otherwise untouched, whether by mechanical or electrolytic polishing. After a deformation of 1-2% in tension neither slip traces nor any other change in the surface, such as distortion of the blocks, could be detected by the electron microscope using the oxide replica technique. After 4% or more of deformation, slip bands were seen crossing the faces and faulting the edges of the cubic blocks. As deformation increased, the number of slip bands and the amount of shear per band both increased until, at large deformations, the whole field of view was covered with slip traces. At all deformations the slip bands tended to cluster together: for example, five bands were sometimes found crossing the face of a single etch block just over a micron in linear dimension. In most cases a fine structure of slip lines could be resolved in each slip band. The slip distance per

elementary slip line was calculated to be 150–200 Å, while the width of the line was 200–250 Å. Thus the authors concluded that each elementary slip line is a region of finite width in which is concentrated localized deformation by an amount of the order of one atom per slip plane. The appearance of a slip band would thus be somewhat as shown in fig. 40 (a).

Fig. 40



Three interpretations of the fine structure in a slip band.

Fine structure in a slip band according to :

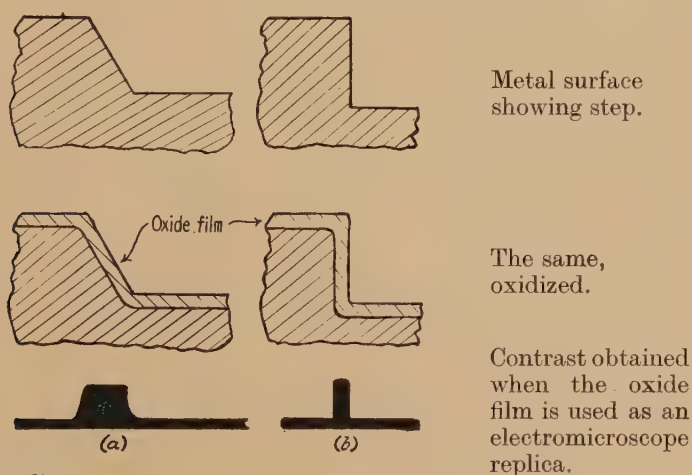
- (a) Yakutovitch and others (1951) and (b) Heidenreich and Shockley (1947) :
 (c) is a compromise between (a) and (b) : (d) is the contrast scheme observed on the electron micrograph in cases (b) and (c).

Now the micrographs produced as evidence by the authors are similar to those of Heidenreich and Shockley and others, apart from differences due to the use of deep etching instead of electrolytic polishing. The interpretation is however different, firstly in that the shear per elementary slip process is only a tenth of what has been assumed in this article,

and secondly in that evidence is produced to show that each elementary slip line is the result of slip, not by a large amount on one active slip plane, but by relatively small amounts on each of about 50 neighbouring atomic planes.

In my opinion the shear per elementary slip process is wrongly calculated, being apparently obtained from the macroscopic strain and the closest band spacing instead of from the average band spacing. This, however, is relatively unimportant if the other result is accepted, namely, that slip within each elementary slip process takes place more or less homogeneously in a zone some 50 atoms wide. With a unit slip distance of 2 000 Å this implies a slip of a dozen atoms per active slip plane. The appearance of a slip band made up in this manner is shown in fig. 40 (c). For comparison, fig. 40 (b) shows the slip band structure

Fig. 41



Contrast in oxide replicas :

- (a) slip plane at an oblique angle to the surface ;
- (b) slip plane perpendicular to the surface.

postulated by Heidenreich and Shockley. It is extremely difficult to decide between the alternatives indicated in (b) and (c) by microscopical methods since the small steps, a dozen atoms high, are far below the resolution limit of any microscope, and the contrast scheme to be seen on electron micrographs is not significantly different in the three cases (fig. 40 (d)). The only way, and the one adopted in the paper considered, is to decide if the slip lines have a finite width.

Now the apparent width of a slip line in the electron microscope using oxide replicas is made up of three quantities (fig. 41) : the true width, if any, of the slip zone ; the projection on the free surface of the exposed portion of the slip plane ; and a quantity roughly equal to the thickness of the film. In some of my experiments on fine-grained polycrystals cases have been found when the slip plane is almost normal

to the surface ; that is, there is no contribution by the slip plane to the apparent width of the line (fig. 41 (b)). Under these circumstances the width measured was about 200 Å—somewhat larger than the estimated thickness of the replica film (100–200 Å). However, the accuracy of the measurement is not sufficient to give a definite answer as to whether the discrepancy is due to a finite width of the slip zone.

If, indeed, slip bands have a profile like that indicated in fig. 40 (c), then the multiplication mechanisms will require modification. The situation would be much like kinking, where it is necessary to explain the propagation of slip to a large number of neighbouring atomic planes, each of which slips by only a small number of atoms. For this reason, the point is worth further experimental study.

§ 6. THE EFFECT OF THE SURFACE ON MECHANICAL PROPERTIES

6.1. *Griffith Cracks*

The Griffith (1920) theory of surface cracks has been successful in explaining the low values of the fracture stresses of brittle materials, in particular of glass. It is supposed that small cracks, mainly on the surface, act as stress raisers ; a relatively small applied stress produces, at the root of the crack, a stress much nearer to the theoretical fracture stress. Amongst evidence for the existence of such cracks there is the observation of Griffith that the fracture stress was much higher for freshly-drawn glass fibres than for similar fibres, the surfaces of which had been 'damaged' by touching gently with a solid body. Reinkober (1931) broke a glass fibre, then the two fragments obtained, then the fragments of the fragments and so on. Because such a process resulted in the progressive elimination of the worst cracks the fracture stress was found to increase as the fragments became smaller. Again, Joffe (1928 b) eliminated the surface cracks on rock salt by continuously dissolving the surface layer. He found that the strength increased by a factor of as much as a hundred.

The calculated depth of Griffith cracks is of the order of a micron. The width at the surface is too small to be observed with the light microscope, but Andrade and Martindale (1935) and Andrade and Tsien (1937) found that metal vapours condensed preferentially on certain lines which could be identified as Griffith cracks (fig. 42, Plate XIX). The cracks have not yet been reliably demonstrated by the electron microscope. Such crack-like objects as have been photographed cannot be distinguished from scratches (fig. 43, Plate XIX).

Attempts to apply a surface-crack theory to explain the low value of the yield stress in metals have been largely abandoned following the success of dislocation theory. Orowan (1948–49), for instance, has summarized the evidence that the yield stress of ductile materials is not determined by the presence of surface cracks. All attempts to raise the yield stress of metals by methods which eliminate surface cracks in

glass have either failed or been proved to be due to impurities. Moreover, the length of the cracks required to explain the yield stress of soft metals like cadmium is often greater than the diameter of the specimen.

Now these observations, and particularly the latter, which is generally regarded as the most cogent objection to a crack mechanism of metallic yielding, do not exclude the possibility that surface cracks or notches may result in a small reduction of the yield stress. In fact, if surface notches can be shown to exist they must act as stress-raisers. The effect on the yield stress may be so small as to go unnoticed in comparison with the usual scatter of values of the yield stress between different specimens.

6.2. Thermal Etching

That a notch structure does exist on the metals was first shown by Graf (1942, 1943) who found a pattern of parallel lines on the surface of metals which had solidified in moist atmospheres. His interpretation of the lines was that they were traces of a lamellar structure existing in the annealed metal. In the hexagonal metals the bounding planes of those lamellae were always slip planes; in the face-centred cubic metals they could be slip planes.

The experiment of Chalmers, King and Shuttleworth (1948) extended the work of Graf and included a careful study of thermal etching of pure silver. After heating in oxygen the silver surface was found to develop a complex structure, sometimes of parallel troughs, sometimes of rows of pyramids. The structure could be removed by heating in inert gases and did not necessarily reappear in the same form as before. The conclusion drawn was that the thermal etch structure was a surface of lower energy than the 'free' surface and was usually made up of $\{111\}$ planes (i.e. slip planes). There was no evidence that it represented any lamellar or other structure within the crystal.

It is obvious that structures such as found by Graf and by Chalmers, King and Shuttleworth must act as surface notches, reducing the yield stress by concentrating the applied stress, even if the effect on the mechanical properties is too small to be observed.

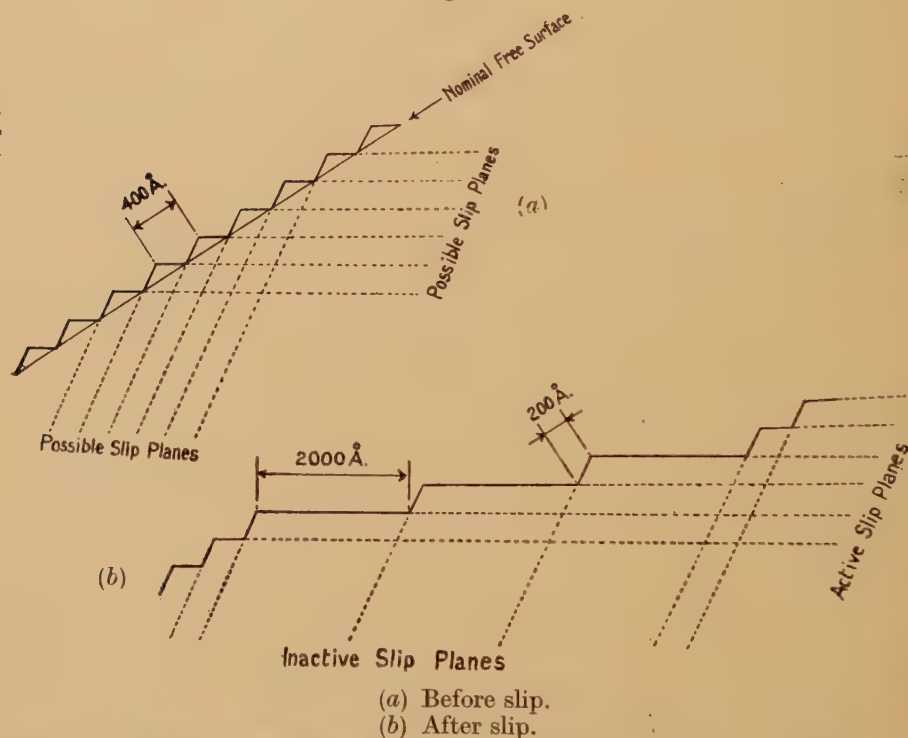
The relationship between the thermal etch structure on cadmium and the slip bands was demonstrated by Andrade and Randall (1950). They heated pure cadmium single crystals under conditions which allowed free evaporation and observed that the surface became crossed by elliptical markings like slip bands. On subsequent deformation it was shown that these markings actually became the traces of the slip bands.

6.3. The Micro-Etch

The electron microscope and electron diffraction have added to the knowledge of surface etch structure. Brown (1950) reported that electron micrographs of pure electropolished aluminium showed a so-called 'micro-etch' structure. This sometimes resembled orange-peel (fig. 44, Plate XIX), but sometimes, depending on the crystallographic nature of the surface, resembled furrows (figs. 24 and 25, Plate

XV). In the latter case the structure was very similar in appearance to, though much smaller than, the thermal etch structure of Chalmers, King and Shuttleworth. Of two adjacent grains, one might show the apparently random orange-peel structure and the other the ordered furrow structure (fig. 45, Plate XIX), and structures of intermediate degrees of order were found. The geometrical relationship of this structure to the slip band was consistent with the view that the furrows were traces of $\{111\}$ planes, that is, of possible slip planes which might or might not become active, depending on the conditions of the applied stress. It was further concluded

Fig. 46



Relationship of the Micro-Etch structure to the fine structure of slip bands.

that the micro-etch structure was a surface of least energy formed in the electropolishing bath when the oxide film was temporarily broken down and some surface migration of metal atoms was possible.

More controversial is Brown's (1950 a) speculation regarding the size of the structure. It was noticed that the period of the structure, that is the distance between adjacent protuberances, was very nearly twice the lamellar spacing. Thus, as shown in fig. 46,* it is possible that the thermal etch notches could be the cause of lamellar formation. Whether

* Figure 46 is reproduced from "Symposium on Metallurgical Applications of the Electron Microscope" (London: The Institute of Metals 1950) by permission of the publishers.

this is true or not it is certain that the micro-etch furrows when parallel to slip bands can be mistaken for slip. A case when this is possible is shown in fig. 47 (Plate XIX). It is probable that misinterpretation of the micro-etch structure led Nishimura and Takamura (1951) to conclude that there was visible slip in the regions between slip bands.

Electron microscopy of electropolished cadmium has also revealed a fine micro-etch structure, the traces of $\{0001\}$ planes and, as such, parallel to slip bands. Here confusion between the two phenomena is much more probable than in aluminium: it is not certain, for example, which of the finer lines in fig. 17 (Plate XIII) are slip and which are micro-etch.

6.4. *The Rehbinder Effect*

There is thus ample evidence that notches exist on metals, but it is impossible, for the reasons stated in § 6.1, to compare the mechanical properties of notched and unnotched specimens. In creep testing, however, it is possible to see the effect of a change of surface conditions on the rate of steady flow of a single specimen.

This experiment was first done by Rehbinder (1947), who discovered that the creep of cadmium crystals was accelerated a factor of 2 or so if the creeping crystal was immersed in certain electrolytes. Rehbinder's view of this was that attack by the electrolyte produced notches in the surface, the traces of basal planes. The notches acted as stress-raisers and so accelerated creep. These experiments have been repeated by Kemsley (1949), Harper and Cottrell (1950), Menter and Hall (1950) and Andrade, Randall and Makin (1950), all of whom agree that the effect is absent if the oxide film is carefully removed from the specimen before the experiment. Now the oxide film is not more than a micron thick; thus it cannot, by its own resistance to tensile stress, strengthen the crystal appreciably. That is to say, if the film were stripped off and placed in the creep machine in parallel with the de-oxidized cadmium crystal its effect on the creep rate would be negligible. In the form of a tough skin on the much softer cadmium crystal however, it can hold up slip at the surface and thus slow down creep.

There is however, a possible interpretation of these results, in line with Rehbinder's ideas. Granted that the effect is in some way due to an oxide film, it may be that the oxide is catalyzing the attack on the surface by the electrolyte. The production of stress-raising notches is thus facilitated and the rate of creep goes up.

The effect of the surface finish on plastic deformation is thus uncertain. What is certain, is that it is not sufficient to query if the surface is giving an accurate indication of internal conditions without at the same time realizing that the surface itself may alter these internal conditions.

6.5. *The Effect of Surface Scratches*

Some experiments by Nishimura and Takamura (1951), which will be described in § 7.7, show that intentional surface scratches, however light, affect the slip-band distribution in their neighbourhood. These results

are particularly important since most specimens for mechanical testing have a few reference scratches, while in some microscopic studies the surface may be criss-crossed with scratches put there to assist micro-location.

§ 7. THE ORIGIN OF SLIP LAMELLAE

7.1. *Slip on Existing Slip Bands*

In § 5 some of the theories to account for the inhomogeneity of plastic deformation were discussed: it appears that there is no theoretical difficulty in creating the number of dislocations required to produce slip by several thousands of atoms on each of a few isolated slip planes. In § 4 it was shown that the spacing of these isolated slip planes can be accounted for only if it is assumed that the disturbance produced in the lattice by slip inhibits further slip in the surrounding region. It has still to be explained why then, as deformation proceeds, slip restarts in existing slip bands, usually on planes displaced a few hundred atoms from the original slip planes.

7.2. *Reality of Lamellar Slip*

The evidence for lamellar slip is based entirely on experiments on the surface. Evidence that slip continues throughout deformation on existing slip planes can be obtained by counting slip bands, as was done by Yamaguchi (1928). A certain amount of evidence that deformation is by discrete amounts, each large compared with the lattice parameter and each occurring in a very short space of time, is available from non-microscopical experiments and has been mentioned in § 2. But the evidence that the discrete amounts of slip making up a slip band are on discrete slip planes, a few hundred atoms apart, is obtainable only from the surface appearance. It is thus worth while considering the possible ways in which such a lamellar structure could be stimulated on the surface without occurring in the interior at all.

It was shown in § 6 that a furrow structure can arise on electro-polished specimens of many metals. Frequently this structure is parallel to the traces of possible slip planes and can easily be mistaken for slip. If now, the metal surface had the property of a skin preventing the slip planes from breaking the surface, as was the case with the mercury crystals studied by Greenland (1937), then in each slip band the furrows give the appearance of slip lamellae.

This effect is shown in fig. 48. Cases have been observed when the surface appears to have acted in this way but these cannot be typical as the furrows are not always parallel to the active slip system. Again in the high temperature-slow strain experiments (§ 2.4; fig. 14, Plate XII) the spacing of the lamellae was much greater than the period of the micro-etch.

However, the furrow structure has, on several occasions been mistaken (§ 6.3) on electron micrographs, for slip in the region between slip bands. Figure 47 (Plate XIX) shows a case where such a misunderstanding is

possible. While it is probable that fine slip does occur in the inter-band regions, it is not in general visible with the electron microscope.

7.3. Coarsening

The spacing of the lamellae in the experiments at high temperatures and slow strain rates likewise shows that they cannot be produced by coarsening (*vergrößerung* as Stranski (1932) called it) of the exposed part of the slip plane. Such coarsening would occur in the manner shown in fig. 49, the small steps being formed by surface migration of

Fig. 48



Simulation of fine structure in a slip band by tilting of a surface skin.

(a) Surface before slip, the furrow structure may not be contrasted in an electron micrograph since both sides of each furrow are equally inclined to the beam.

(b) Surface after slip, slip on one slip plane has tilted the surface skin. Within the profile of the slip band the sides of each furrow are unequally inclined to the electron beam and will be contrasted.

Fig. 49



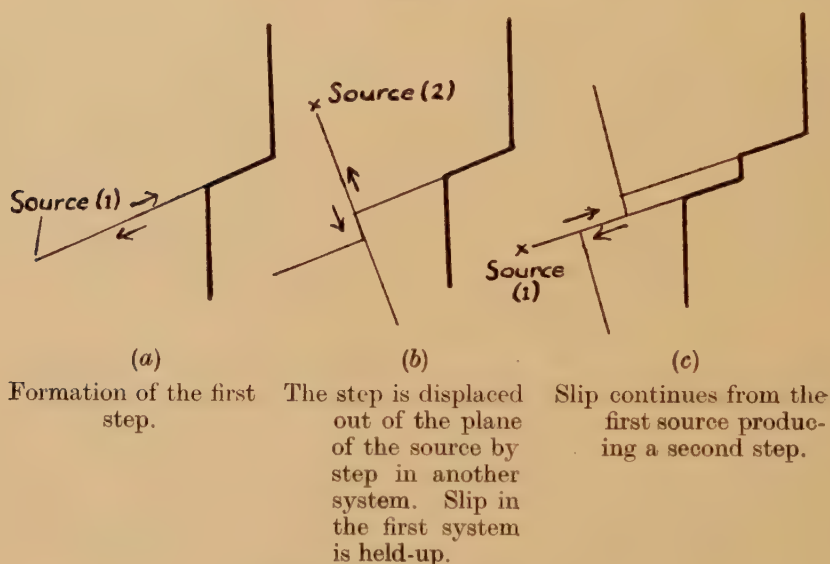
Simulation of fine structure in a slip band by coarsening of the newly exposed surface.

atoms to form a surface of lower energy than the slip surface. In room temperature deformation such migration is impossible without the aid of an electrolyte, but since most electron micrographs of fine structure in slip bands are obtained from electrolytically prepared replicas it is as well to show that the lamellar structure is seen on replicas prepared by other methods. Figure 44 (Plate XIX) shows where fine structure has been resolved in a slip band on an aluminium polycrystal by a plastic replica method (Brown (1950 b)). This figure also shows a case when the micro-etch structure is of the orange-peel type and has no relationship to the slip band.

7.4. Lamellar Slip as a Sub-surface Phenomenon

Cottrell (1952) has recently suggested that the whole of the slip making up the slip band takes place on one slip surface, at least in the neighbourhood of the source, and probably over most of the interior of the crystal except in the layer immediately under the surface. As slip approaches an obstacle, which might be the free surface or perhaps a kink band, the slip is divided out over a number of closely spaced parallel slip planes and appears on the surface in the form of a cluster of lamellae. The transference of the slip from plane to plane takes place by slip on another set of planes in the manner shown in fig. 50. On the usual criterion of maximum shear stress the latter set would remain inactive but is now made active locally by the stresses of the dislocations held up at the obstacle in much the same way as slip takes place within a kink band, on planes inclined to the ordinary slip system. Alternatively, slip could be transferred from plane to plane by cross-slip in the manner

Fig. 50



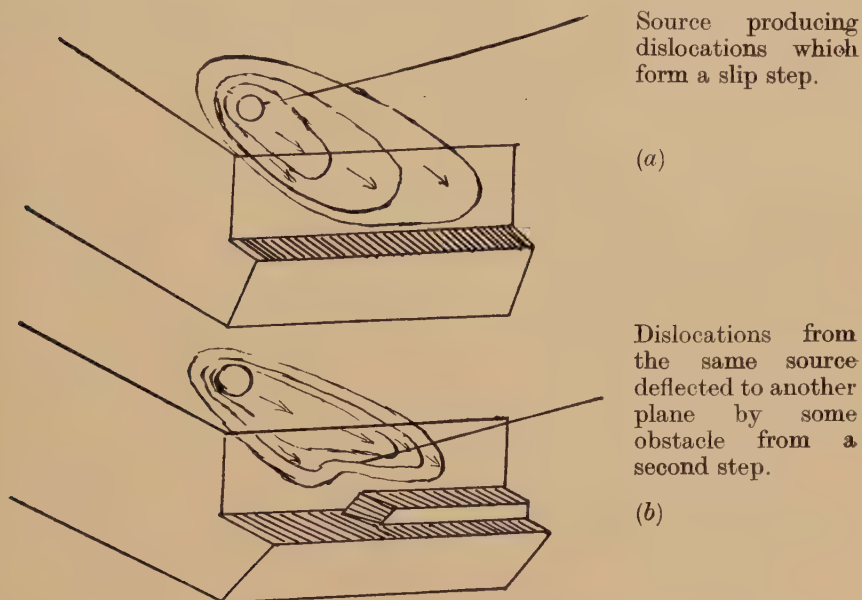
Formation of fine structure.

shown in fig. 51. Once again an obstacle is required in the path of the advancing slip front. This mechanism can explain the temperature effect; at higher temperatures there is more slip on each slip band, because hardening is less and at the same time cross-slip is more frequent, both between bands (fig. 9, Plate XI) and within bands (fig. 14, Plate XII).

A positive piece of evidence for Cottrell's suggestion is the observation that as a slip process approaches an obstacle it does in fact spread out. It is not, of course, possible to see microscopically what happens to a slip band as it approaches a surface, but is frequently observed that in

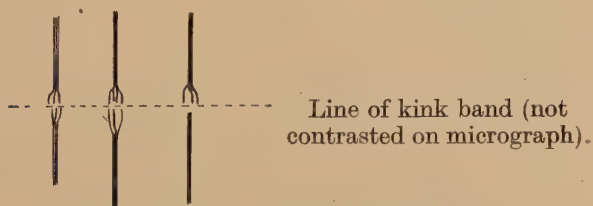
the neighbourhood of a kink band the lamellae are much more widely spaced than usual (figs. 52 and 53, Plate XVII). Kink bands are not contrasted in the electron microscope but can be recognized as the locus of such impediments to slip (see fig. 54).

Fig. 51



Fine structure formed by cross-slip.

Fig. 54



Behaviour of slip bands at intersections with kink bands.
(See Plate XVII, figs. 52 and 53.)

Cottrell's mechanism is designed to avoid two of the difficulties which arise in the theoretical justification of lamellar slip. The first of these is the special distribution of Frank-Read sources which is required if each lamella had its own source; in Cottrell's mechanism all the lamellae come from the same source. Secondly, there is the difficulty of explaining how a slip process can be forced across a slip plane so close to a former slip plane, right through the hardest region. As to the former, some reasons have already been given (§ 5.4) why all lamellae must come from

the same source. The latter however, involves the assumption that slip is not stopped by hardening on an active slip plane, for if it were, the stress to restart on the same plane would certainly be no less than the stress to start a new slip plane a hundred or so atoms away.

Cottrell's mechanism thus implies slip, not in jumps as was assumed in § 2, but continuously on each active slip plane. Once the stress is sufficient to start a Frank-Read source operating, it continues to create dislocations and these continuously migrate towards the surface as long as the stress is applied. These dislocations are held up by some obstacle and not released until sufficient have collected (about 700 apparently in the case of aluminium) to raise the stress locally to a value required to operate the mechanism of transfer to another slip plane. They then appear on the surface as a 2 000 Å step. Thus for every slip band visible on the surface there is also on the average an extra slip distance of the order of half the lamellar slip distance, concealed under the surface. This concealed slip makes the macroscopic strain more than can be measured by measuring the height of slip steps. At large strains when the slip distance per band is of the order of a micron the concealed slip may be too small a fraction of the total to be detected, but at small strains there ought to be markedly more strain than can be accounted for by the visible slip bands. Now Yamaguchi could not detect any slip lines until the strain was about 1% when a number of the order of 50 per mm suddenly appeared. Again, in the experiments of Kurnosov, Tronina and Yakutovitch, referred to in § 3.4 it is possible that part of the invisible strain could be accounted for in this way.

The inference is that the slip processes had been held up under the surface pending the arrival of sufficient dislocations to force an exit. It may also be that by chance, the number of held up dislocations required to operate Cottrell's mechanism is almost constant for aluminium but is not so constant for other metals. This would explain the apparent regularity of the slip distance in aluminium.

Now the dislocations thus held under the surface should be still mobile and thus it should be possible to recover the fraction of the strain they represent by reversing the stress. If this process of 'unslipping' is not detected, it may be because there are also internal obstacles, such as kink bands preventing the dislocations from running back (§ 8.3).

Cottrell's theory depends on the circumstance that slip can jump from plane to plane. If cross-slip or any other slip phenomenon which gives the effect of non-straight slip bands is unlikely, the effect of the surface hold up should be to stop, or slow up, slip on the slip band in question and transfer it to another. Thus when slip bands are habitually straight, there should be fewer lamellae per band and more bands, corresponding to a given strain. This is exactly as is found in impure materials and at low temperatures. Again, some of the most striking examples of banding occur in the hexagonal metals where transfer of slip from plane to plane must be rare since there is only one slip plane. Cases of apparent cross-slip in cadmium are shown in figs. 18 and 19 (Plate XIII) but these,

together with others from the same specimen are the only recorded cases of cross-slip in a hexagonal metal. The case of tin will be referred to in § 8.5 where it will be shown that, when tin behaves as a hexagonal metal (single crystal specimens), there is banding but no cross-slip; whereas when tin behaves as a cubic metal (polycrystalline specimens) there is an abundance of cross-slip but no banding.

The theory has, as yet, given no clear idea as to the nature of the obstacles to slip. It seems unlikely that any obstacles could be equally effective at 500°C and at -180°C , but in fact the lamellar distance, which has been interpreted as a measure of the resistance of the obstacles, increases slightly with temperature. Again, in impure metals, where a greater accumulation of dislocations would seem to be required to force the surface, the lamellar distance is, in fact, less.

If it is correct that slip within a band is on one atomic plane only, then in cases when the free surface of the metal contains the direction of slip, the width of the band should be unresolvably small. In fact the width of such a band, as seen at points where it has faulted some surface mark, is always a few hundred ångström units. This is shown in fig. 55 (Plate XVII), where two slip bands of measurable width with their slip directions almost in the free surface have faulted a set of bands almost perpendicular to the surface. However, neither in this case nor in any other cases which have been observed of slip parallel to the surface, can the small steps corresponding to the lamellae be resolved in the faults.

7.5. *A Recovery Mechanism for Lamellar Slip*

An alternative explanation of the origin of lamellar slip has been proposed by Brown (1951). In this, the surface appearance is taken to be a true indication of the situation within the metal; that is, the lamellar slips retain their individuality (though not necessarily their parallelism) right through, and represent each an avalanche of slip taking place in a very short interval of time. The avalanche is started when the applied stress is sufficient to set off some process of dislocation multiplication and stopped by work hardening. The same work hardening which stops the slip avalanche is also the cause of the macroscopic hardening of the crystal, since the spacing of the slip bands is determined by interaction between them. That is, it is assumed that the disorder resulting from the passage of a slip avalanche produces stresses in the surrounding metal, causing it to become harder in the sense that higher stress is required to force another slip process through it. The greatest resistance to slip is close to the slip band; thus the most probable site for the next slip band is about midway between existing bands. In order to account for the observed fact that slip also occurs on planes very close to, but not coincident with, existing active slip planes, it is suggested that the region around slip bands becomes a region of easy slip as a result of recovery. The fundamental assumption is that, in the most highly stressed parts of lattice, little temperature activation is required to produce recovery.

The assumption that there is interaction between slip bands several microns apart and the assumption that there is recovery in the interband region both require the presence of dislocations off the slip plane. For if all dislocations were concentrated on the slip plane, then it has already been shown (§4.7) that the distance over which hardening is effective is much less than the distance between slip bands. Secondly, under such conditions, recovery of the stresses in order to permit slip on the lamellar sites would require recovery on the slip former plane itself and hence, since removal of the source of stress involves removal of the stress everywhere, recovery throughout the region between slip bands. Thus, with dislocations only on the once active slip planes, there would, after recovery be no preference for slip on planes close to slip bands. The evidence for the existence of dislocations in the interband region, as well as a suggestion of their origin, have already been given in § 5.6.

The effect of the temperature of deformation on the slip bands is explained by the recovery hypothesis as follows: The critical stress required to produce self-annealing depends on temperature. At high temperatures, thermal activation assists the onset of self-annealing and thus, at high temperatures, slip close to existing bands takes place at very small strains. At the temperature of liquid air, and more so at the temperature of liquid helium, the stresses producing self-annealing are not helped by temperature and thus lamellar slip is not found until strains of the order of 40–80% are reached. (Compare fig. 2 (Plate X) where the deformation was 20% with fig. 55 (Plate XVII) where the deformation was over 80%.)

The annealing mechanism has been invoked to explain the phenomenon of lamellar slip, that is slip within existing slip bands but not on the original slip plane. It is not of course, necessary that the new slip planes should be resolvably distinct from the older ones, nor indeed, does it appear necessary that they should be distinct at all. All that is required is that slip, once started on a slip plane, must stop after a more or less definite amount has occurred and restart when conditions become more favourable later. Thus, in order to justify the process, it is necessary, not to resolve lamellae in all metals, but to show that deformation is fundamentally jerky, as it was in Joffe's and Holden's experiments (§ 2.4). The requirement that the slip process must create dislocations in the region between slip bands appears necessary to explain band spacings and it appears, on the basis of the reasoning in §§ 5.5–5.6 that a dynamic (i.e. avalanche) slip mechanism is more likely to put them there than a mechanism of more sedate continuous slip.

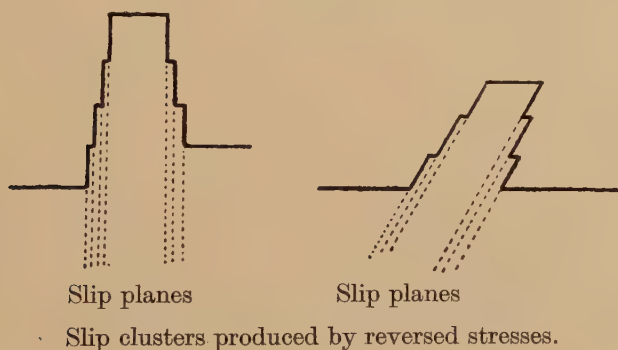
7.6. *Slip Bands as Sites for Easy Slip*

In both Cottrell's and Brown's mechanisms, slip bands are surfaces on which slip is easy. In Cottrell's mechanism the reason for this is that a source of dislocations has started operation and should continue to operate there as long as the stress is applied. In Brown's mechanism

the softness of the slip bands is due to recovery. If now, the applied stress is reversed, the source in Cottrell's mechanism is sending out dislocations of the wrong sign and thus the original slip band is unlikely also to be a site for slip on the same crystallographic slip planes, but in the reverse direction. In Brown's, however, the parts of the crystal softened by recovery should be available for easy slip in either direction.

Now it is found that in specimens deformed in alternating stresses some of the slip bands are not staircases, as in unidirectional stress, but stiles. That is, all the steps do not go the same way. This is shown in fig. 56 (Plate XX) which is from an aluminium polycrystal deformed by bending and then straightening again. The steps 'up' (black) have been distinguished from the steps 'down' (white) by shadow casting; the beam of evaporated metal has piled up against the rising parts but has cast a shadow from the falling parts. The appearance of these slip stiles is shown schematically in fig. 57. On a larger scale it turns out that in such a specimen there are slip clusters composed only of 'rising' lamellae, others composed only of 'falling' lamellae, but a large number, too large to be the result of chance, are composed of a mixture.

Fig. 57



7.7. Slip Bands formed by Fatigue Stresses

It is not a new hypothesis that active slip planes are planes of weakness for it is known that slip planes can develop until fracture takes place on them (Orowan (1948-49)). A particularly elegant demonstration of this has recently been produced by Duce (1951) who studied slip lines on specimens of nickel, copper, magnesium, aluminium, etc., subjected to alternating torsional stresses. A series of Dr. Duce's photographs of the same area of a nickel polycrystal at various stages of such a test are reproduced in figs. 58-66 (Plates XXI and XXII). Figure 58 shows the specimen at the start of the test, electro-polished and undeformed. In fig. 59 (5 000 cycles) fine slip bands have appeared, apparently in directions unrelated to the maximum shear stress. In fig. 60 (10 000 cycles) those bands most favourably placed in relation to the applied stress have begun to broaden, that is more slip has occurred

on them. As the number of cycles increases, very few new bands are formed but the shear on each increases steadily until, just before fracture (fig. 65—270 000 cycles), the slip bands are very broad and resemble cracks. Figure 66 (not from the same area) is a picture of part of the main fracture and shows that, while the final fracture is mainly intercrystalline, some transcrystalline fracture and subsidiary cracking has taken place on former slip bands. (Note in connection with fig. 66 that slip bands in the region of fracture have been produced under conditions of very inhomogeneous stress and thus need not be oriented according to the apparent direction of maximum shear stress.)

Figures 67 and 68 (Plate XXII) show electro-micrographs on slip bands on aluminium specimens which have been similarly fatigued. Since the preparation of these micrographs involved destroying the specimens it is not possible to show a series at different numbers of cycles, but it is clear that the extra shear on each band appears in the form of new lamellar slip processes, that is as a result of one or other of the mechanisms under discussion.

Figure 68 shows in addition how slip by a large amount on a slip band in one grain, if it cannot pass easily into the adjoining grain, distorts the grain boundary, leading perhaps to intercrystalline failure. In the magnesium specimens where there is only one slip plane per grain this effect is particularly striking and leads to intercrystalline cracking at an early stage in the test. (Figure 69, Plate XXII.)

7.8. *The Effect of Local Slip*

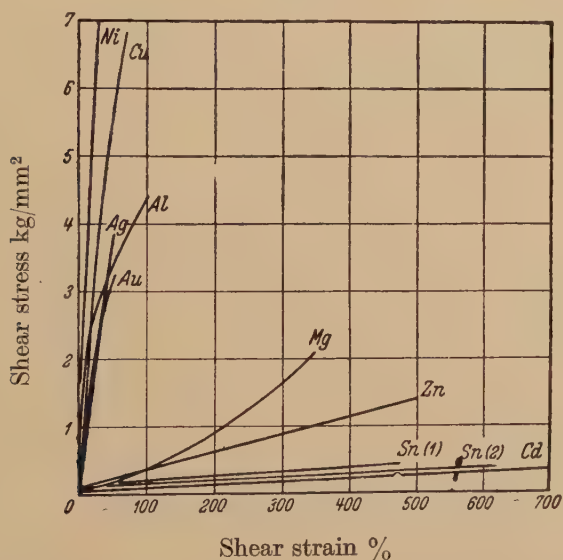
Since the effect of slip is to harden a metal and at the same time, apparently, to produce paths of easy slip it is interesting to note the effect of slip occurring purely locally. Such slip is seen at the edges of fine scratches (fig. 70, Plate XX), as well as around such local surface damage as hardness indentations.

Nishimura and Takamura (1951) made scratches, estimated to be about 10 microns deep, on otherwise undeformed aluminium single crystals 1.5 mm thick. When the scratch was perpendicular to the direction of the expected slip traces subsequent extension of the crystal revealed a very slight increase in the density of slip bands in the neighbourhood of the scratch (fig. 71, Plate XX). If the scratch was parallel to the expected direction of slip bands then there was a clearly marked region on either side of the scratch, free from slip bands (fig. 72, Plate XX). This region also appeared on the under- (unscratched-) side of the crystal.

The probable reason for this effect is shown in fig. 70 (Plate XX) which was obtained in collaboration with Whitehead (1950) and shows a fine scratch made on aluminium by a steel slider carrying a load of only 50 mg. Fine slip lines have been produced locally on either side of the scratch and the active slip planes are at about 45° to the direction of scratching. Now these slip bands harden the region they pass through, but at the same time each is a site for further slip, that is a soft plane

in the midst of a hardened region. So if the slip producing extension can occur on these planes it will do so, resulting in little change in the distribution of slip bands. If, however, the slip planes made active by the tensile stress are not these planes of local slip, then slip is inhibited in the region round the scratch, for this region is already hardened and the only soft planes in it are in the wrong direction. A consequence of this is that the crystal should be slightly harder for slip on latent slip systems than on active slip systems. The opposite result was obtained by Röhrl and Kochendörfer (1950) who deformed single crystals of aluminium by pure shear on one set of slip planes, then sectioned the specimen in order to be able to measure the resistance to shear on another set. While the latter experiments give an apparently more direct result it is to be doubted if sectioning soft crystals with a saw has not affected the result.

Fig. 73



Stress-strain curves for various metals. [*E. Schmid and W. Boas* (1935).]*

§ 8. SLIP PROCESSES AND WORK HARDENING

8.1. Single Crystals

One of the best known diagrams of metal physics is that due to Schmid and Boas (1935) which shows that the stress-strain curves of metal single crystals fall into two clearly marked groups. This is reproduced in fig. 73 and shows that the cubic metals work harden at a much greater rate than the hexagonal metals. A fairer comparison than this can be made if the stress-strain curves are plotted, not all at the same absolute temperature, but at the same temperature for each, relative to its melting

* Figures 73, 74 and 75 are reproduced from 'Plasticity of Crystals' (London 1950 : F. A. Hughes & Co.), Ltd., by permission of the publishers.

point; this brings the two groups closer together but still leaves them sharply defined.

If the evidence of § 2 is accepted, there is a corresponding difference between the slip processes in the two groups: in the cubic metals slip is on many closely spaced slip bands, each of which slip by only a few thousand atoms. In the hexagonal metals, most of the slip bands appear early in the deformation and increase in shear throughout. In each case the total slip in a band is divided between lamellar slip planes, many in the case of the hexagonal metals, few in the case of the cubic metals. Without accepting any explanation of why the total slip in a band should be so divided, it seems reasonable (§ 5) to assume that it all comes from the same source. Therefore in the hexagonal metals, a few sources are able to supply unlimited numbers of dislocations, most of which can leave the surface even to the extent of causing fracture on the slip plane. The small amount of hardening observed suggests that few dislocations are retained in the interior. In the cubic metals however, dislocations accumulate on and around active slip planes until densities of the order of one per thirty atoms are reached. That is, in the cubic metals the number of trapped dislocations per millimetre of slip plane is about 10^5 .

8.2. *Polycrystals of Cubic Metals*

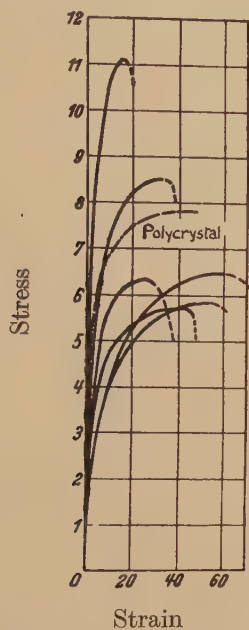
The interest of this estimate for the density of dislocations lies in the comparison of the stress strain curves for single and polycrystals of the same metal with the behaviour of slip bands in each case. Figure 74, also due to Schmid and Boas, shows that for a cubic metal (aluminium) the rate of strain hardening does not differ markedly from large single crystals to fine grained polycrystals (experiments on single crystals deformed in pure shear are excluded and will be considered later). This may be taken to indicate that the density of trapped dislocations is the same over the whole range of grain size. Thus, for a given strain, there are perhaps a hundred times as many dislocations trapped on the long slip planes of the single crystal as there are on the tiny slip planes of the polycrystal. In spite of this the slip distance per band, that is the number of dislocations escaping to the surface, does not vary by as much as a factor of five over the whole range of crystal size if the regions of complex slip close to grain boundaries are excluded. Thus, in the cubic metals, the number of dislocations emerging from the surface is almost independent of the size of the pool of dislocations from which they are drawn. An explanation of this could be that the surface acts as a gate, opening under a certain pressure of dislocations, in much the same way as Cottrell proposed to explain the origin of slip lamellae (§7.4). This, however, leaves the problem of what closes the gate again when some 99% of the dislocations behind it are still left inside. A more likely suggestion is that the dislocations which break surface are drawn, not from the whole slip plane but only from a part of it close to the surface. The length of this part will be of the order of magnitude given by

$$l \sim s \cdot n,$$

where s is the spacing of dislocations on the slip plane and n is the number emerging on the surface. With the values assumed above l is about 3×10^4 atom spacings or about 10 microns.

Since the amount of slip must be of much the same amount at all parts of the slip plane, and since it is improbable that a crystal or a crystalline grain could consist of a kernel where slip is by unlimited amounts separated from the surface shell by an impenetrable wall, the above argument suggests that the whole crystal is divided up by walls impermeable to dislocations and of distance l apart.

Fig. 74



Stress-strain curves for aluminium single crystals of various orientations.

For comparison: a stress-strain curve for a polycrystal of aluminium.
[*E. Schmid and W. Boas (1935).*]

8.3. The Nature of Dislocation-proof Walls

The suggestion that a metal was divided into compartments by impermeable walls perpendicular to the slip planes was first made by Taylor (1934) to explain work-hardening. In his model the walls existed already in the annealed metal and were not altered during deformation. There were dislocations in each compartment which could move freely under the action of the applied stress within their own compartment, but which could not pass into another compartment. Strain hardening was accounted for by assuming that the number of dislocations in a compartment increased during deformation by a process of creation at the walls and that the movement of each dislocation under the applied stress was made increasingly difficult by the increasing stress-field of the others.

Taylor's mechanism involved many assumptions which are not readily justifiable in the light of modern experimental results but gave an expression for the stress-strain curve which agreed fairly well with experiment. Orowan (1951) has recently summarized the main objections to Taylor's theory; one of the most serious is that the obstacles to slip are supposed to pre-exist in the undeformed crystal and are not, as is generally believed now, the result of injuries to the lattice during deformation. There was also no experimental evidence for the existence of such walls at any stage during plastic deformation; they cannot, for example, be identified with the boundaries of mosaic blocks since it is observed that slip can pass apparently undisturbed across any such boundaries.

It is natural today to identify the impermeable walls postulated above with kink bands, the properties of which have been described by Honeycombe (1951). These kink bands are regions of lattice curvature formed during deformation on planes perpendicular to the slip planes. They are apparently impermeable to slip for Honeycombe has shown that slip bands which are formed subsequent to the appearance of the kink band do not readily pass through it. Similarly, it was shown by repolishing the specimen after the appearance of kink bands that old slip bands did not, when they reappeared, pass through either. The spacing of kink bands varies from about 3μ for 20% extension of a 99.5% Al crystal to about 10μ for a similar extension of a 99.95% Al crystal.

In general, according to Honeycombe, the kink band spacing is wider and less regular the purer the specimen; this is in agreement with the suggestion that the visible slip bands arise from a region near the surface of size

$$l \sim s \cdot n,$$

since the shear on a slip band, which is proportional to n , is less in the less pure materials.

Honeycombe has also investigated the effect of temperature and speed of deformation on the kink bands; the spacing was found to be 2-3 times greater on a specimen deformed quickly at 450° c than on one similarly deformed at room temperature. It is well known that the slip-band spacing, i.e. the shear per slip band also increases with temperature and while the effect of temperature of deformation on the dislocation spacing is not known, these results are in qualitative agreement with the suggestions above.

For the effect on the kink-bands of speed of deformation, the evidence is more contradictory. While there was little difference between the kink bands developed on specimens of 99.5% Al deformed at room temperature, one quickly, the other at $\frac{1}{2}$ % per day, there was a great difference between specimens of high purity Al deformed at these rates at 300° c. The specimen deformed slowly at 300° c developed prominent, widely spaced bands. Now it is known that slip bands developed in high speed deformation are a little closer spaced, i.e. have less shear per band at room temperature than if they had been formed at slow rates but the difference

is not large (§9). Probably it is not large enough to make a noticeable difference in the kink band spacing. On the other hand, under conditions of very slow strain and high temperature slip bands have been shown (§2.4) to be very widely spaced and to represent enormous shears.

8.4. *Crystals without Kink Bands*

Honeycombe has shown that the appearance of x-ray asterisms in deformation can be ascribed to kink bands. In the cubic metals, no matter how carefully the single crystals were handled and deformed in tension, x-ray asterisms and kink bands appeared in the first few per cent of deformation. In the hexagonal metals, on the other hand, asterism in single crystals was not found by sensitive x-ray methods unless the crystals were deliberately bent. The absence of x-ray asterisms was found to correspond to an apparent absence of kink bands. If then, kink bands are alone responsible for preventing dislocations from leaving the crystal one would expect to get much greater amounts of shear per slip band in the hexagonal metals than in the cubic metals, and at the same time much less hardening for a given strain since a much smaller fraction of the dislocations formed during the deformation will have been trapped in the interior.

8.5. *Polycrystals of the Hexagonal Metals*

Figure 74 shows that a polycrystal of a hexagonal metal (magnesium) work hardens at a much greater rate than a single crystal of any orientation. The actual rate is comparable with that for the cubic metals. The slip bands on hexagonal polycrystals are correspondingly fine and closely spaced like those on cubic metals, and the reason for this is that unlimited slip cannot occur on any one slip band because of obstructions by neighbouring grains. The process is as follows: slip begins on a slip band when a source of dislocations is activated there by the applied stress. The dislocations created make for the grain boundary and some are able to pass out if the next grain can deform a little. Since there is only one slip plane such accommodation by neighbouring grains is limited and all further dislocations on that plane must remain within the grain and contribute to the work hardening. The stress rises, activating more sources and thus the number of bands grows.

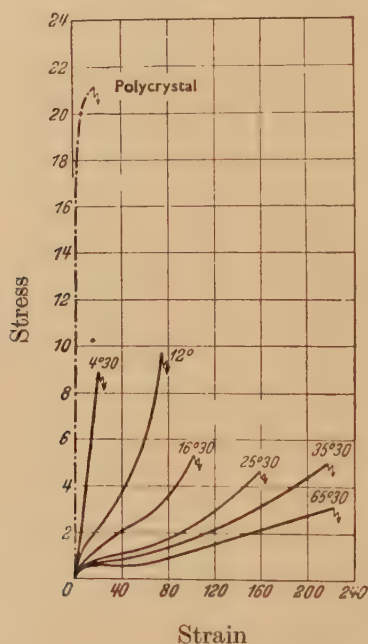
This process is illustrated in figs. 20–22 (Plate XIV) which are electron micrographs of slip in tin. This metal is not hexagonal, but a single crystal behaves as a hexagonal metal; that is to say, in the absence of twinning it deforms on one set of slip planes and has a stress strain curve belonging to the lower group (fig. 73). In fig. 20 (Plate XIV) it is shown that the slip bands from a single crystal are widely spaced and resolvable into clusters exactly as in single crystals of cadmium. Figure 21 is an enlargement of such a complex band. In polycrystalline tin, large amounts of slip on widely spaced bands are not possible but tin, unlike cadmium, has other equivalent slip systems available and

slip takes the form shown in fig. 22. This fine, closely spaced branched slip corresponds to a high rate of work hardening.

Now while polycrystals of the hexagonal metals certainly show x-ray asterisms after plastic extension it is not recorded whether they also show kink bands. However, Honeycombe's experiments make it reasonable to believe that they would. If so, the correlation is complete between the presence of kink bands and the amount of slip which emerges from the surface.

In the experiments of Röhm and Kochendörfer (1950) it was shown that single crystal of aluminium deformed in pure shear did not develop x-ray asterisms. Thus, on Honeycombe's reasoning there are no kink bands. Since Röhm and Kochendörfer did not polish their specimens it

Fig. 75



Stress-strain curves for magnesium single crystals of various orientations.

For comparison: a stress-strain curve for a polycrystal of magnesium.

[*E. Schmid and W. Boas (1935).*]

is not possible to say definitely what is the effect of this type of deformation on the slip bands but their published photographs of unpolished specimens suggest that slip was confined to a very few bands. With the mechanism above, this means that an unusually large proportion of the dislocations formed during the deformation were able to leave the crystal and consequently that the work-hardening should be less than in specimens deformed in the usual tensile apparatus. In fact they found that it was.

§ 9. THE EFFECT OF THE RATE OF STRAIN ON SLIP PROCESSES

If the temperature of deformation is kept constant, it is found that very slow deformation results in the appearance of slip bands which are more widely spaced and broader than those formed at normal rates of mechanical testing. That is, reducing the speed of deformation results in there being more shear within each slip band. Comparison of figs. 13 and 14 (Plate XII) with figs. 5 and 6 (Plate X) shows that in the case of, aluminium at least, this extra shear takes the form of an increase in the number of lamellae within the band.

However at strain rates far above those used in ordinary tensile testing the situation is not so clear. It has been reported, for example by Parker and Smith (1944) and by Crussard (1945), that with very fast rates of extension such as are obtained in impact testing, the slip bands, while closely spaced, appear to be broad and to involve a large number of active slip planes. There are few confirmatory experiments but figs. 76 and 77 (Plate XXIII) show results of experiments on aluminium single crystals extended 4% at strain rates of about 100 per sec at room temperature. With normal rates of strain such conditions would produce slip bands spaced about 10 microns apart and each containing one or two of the usual 2 000 Å lamellae. Here fig. 77 shows that the slip band spacing is from $\frac{1}{2}$ to $1\frac{1}{2}$ microns while fig. 76 (not from the same crystal) shows the resolution of one of the bands. There are four lamellae and the slip distance for each is well under 1 000 Å. The great majority of slip markings formed in this way however, are not resolvable but appear simply as broad bands.

Thus at very high rates of deformation slip processes are more readily transferred to neighbouring slip planes and less slip is observed on each active slip plane. This is very similar to what takes place in kinking and in the punch effect (§ 5.5) both of which are also examples of deformation which takes place extremely rapidly.

ACKNOWLEDGMENTS

I wish to thank all who have kindly lent me photographs. Acknowledgment to them is made in the captions to their pictures. In some cases where the pictures have been previously published I also wish to thank the publishers for permission to reproduce.

Particular thanks are due to Professor A. H. Cottrell, Dr. A. G. Duce and Dr. J. Holden who have allowed me to use their unpublished results.

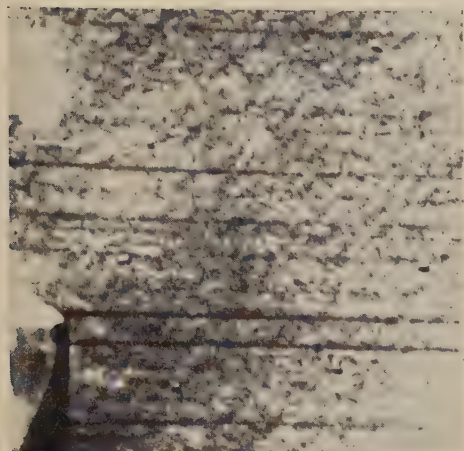
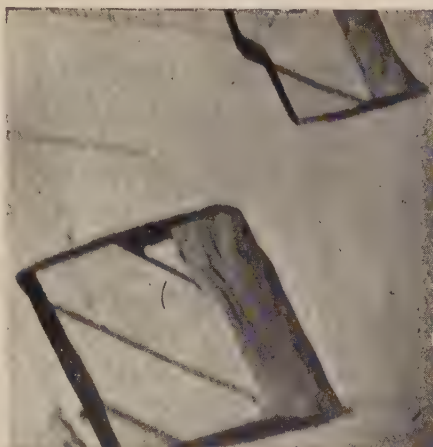
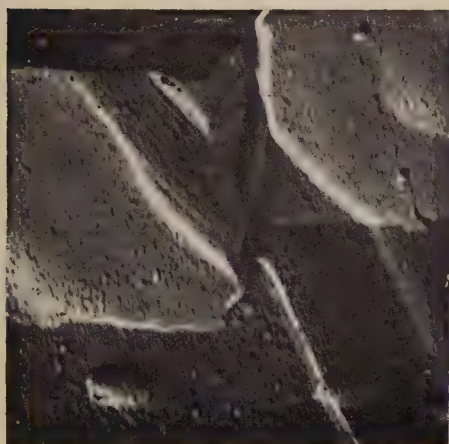
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SLIP IN ALUMINIUM AT VARIOUS TEMPERATURES

Fig. 1. -270°C. $\times 20\,000$ Fig. 2. -180°C. $\times 10\,000$ Fig. 3. 20°C. $\times 25\,000$ Fig. 4. 250°C. $\times 15\,000$ Fig. 5. 350°C. $\times 20\,000$ Fig. 6. 500°C. $\times 24\,000$

All specimens were deformed quickly to approx. 40% shear strain. Figs. 1-6 are electron micrographs from aluminium oxide replicas.

[Figs. 2, 4 and 6 are reproduced by courtesy of the *Institute of Metals*.]

CROSS-SLIP

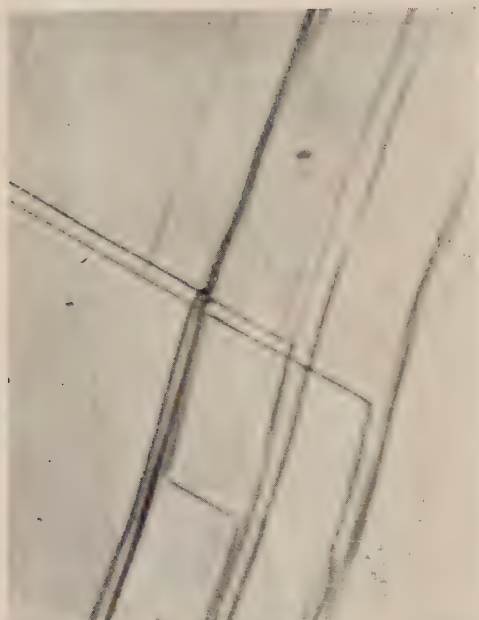


Fig. 7. Prominent cross-slip in α -brass, 0.09% strain. $\times 2\,000$

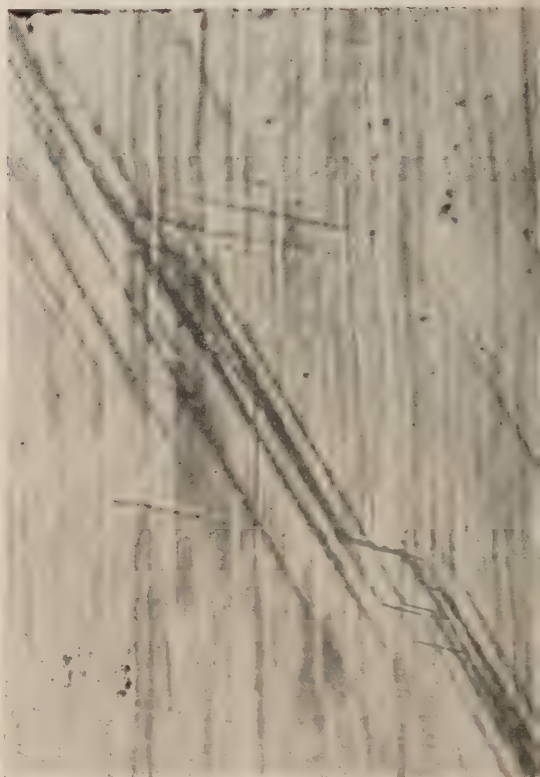


Fig. 8. Intimate cross-slip in α -brass, 0.1% shear strain. $\times 1\,000$

[Figs. 7 and 8 are by R. Maddin, C. H. Mathewson, and W. R. Hibbard and are reproduced by courtesy of the American Institute of Metals and Metallurgical Engineers.]



Fig. 9. Aluminium crystal extended 9% at 400°C. $\times 100$

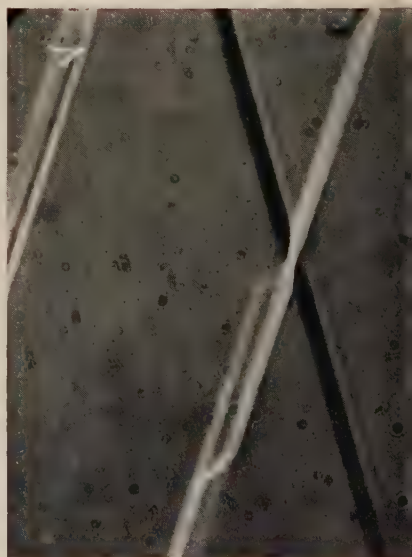
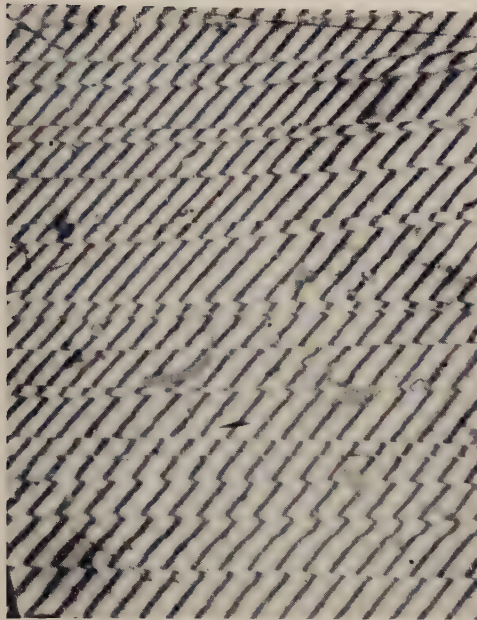


Fig. 10. Aluminium single crystal extended 5% at room temp. $\times 2\,350$

[Figs. 9 and 10 by R. W. Cahn. Fig. 10 is reproduced by courtesy of the Institute of Metals.]

CONSTANCY OF THE ELEMENTARY SLIP DISTANCE IN ALUMINIUM

Fig. 11. $\times 110$ Fig. 12. $\times 110$

Figs. 11 and 12. Aluminium single crystals extended (fig. 11) 0.5%, and (fig. 12) 1% showing displacement of multiple beam interference fringes by slip.

[Figs. 11 and 12 by *J. Holden.*]



Fig. 13. Large slip bands on a single crystal of aluminium deformed 12% at 450°C at a constant strain rate of 1% per day. $\times 6$



Fig. 14. Part of the fine structure of one of the slip bands in fig. 13. Electron micrograph from shadowed oxide replica. $\times 25\,000$

[Fig. 13 by *R. W. K. Honeycombe.* Figs. 13 and 14 are reproduced by courtesy of the *Institute of Metals.*]

SLIP IN CADMIUM



Fig. 17. Fine structure in a slip band on a cadmium single crystal. $\times 25\,000$

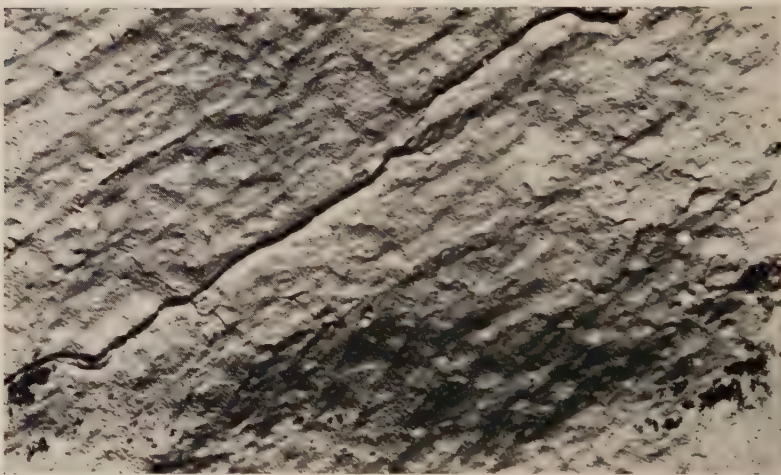


Fig. 18. Cross-slip on a cadmium single crystal. $\times 15\,000$

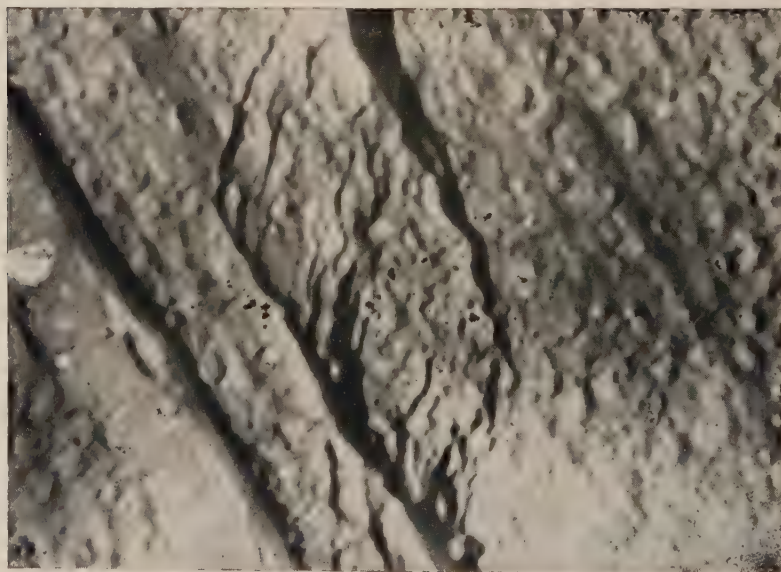


Fig. 19. Cross-slip on a cadmium single crystal. $\times 15\,000$

[Figs. 17, 18 and 19 are electron micrographs from replicas by the polymerization process.]

SLIP IN TIN



Fig. 20. Widely spaced slip bands on a tin single crystal. $\times 10\,000$

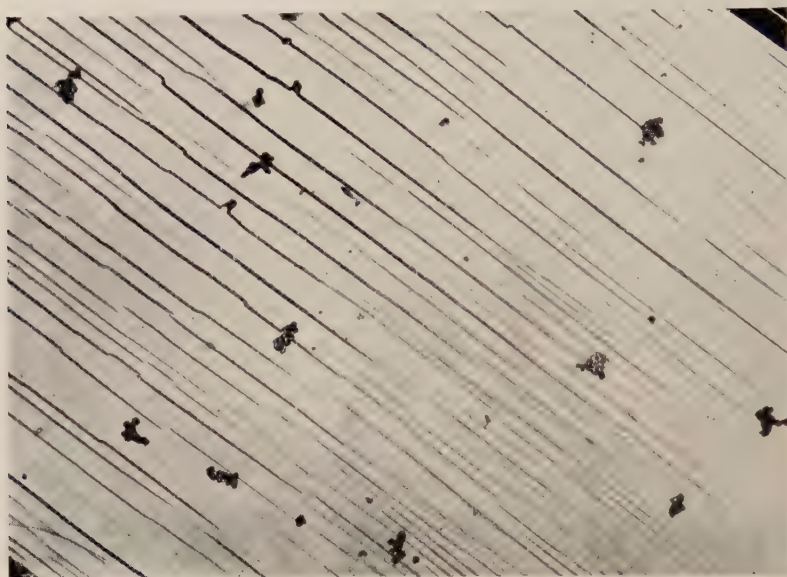


Fig. 21. Fine structure in a slip band on a tin single crystal. $\times 35\,000$



Fig. 22. Slip and cross-slip on a tin polycrystal. $\times 10\,000$

[Figs. 20, 21 and 22 are electron micrographs from replicas by the polymerization process.]

EFFECT OF THE METHOD OF PREPARATION OF THE SURFACE
ON THE APPEARANCE OF SLIP BANDSAbraded
zone.Unabraded
zone.Fig. 23. Transition
region on an
aluminium single
crystal. $\times 250$

[R. W. K. Honeycombe.]

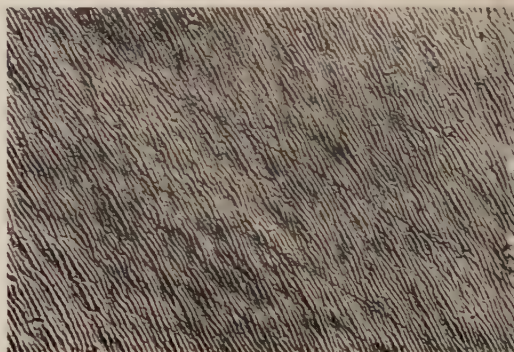
Fig. 24. $\times 10\,000$ Fig. 25. $\times 10\,000$ Figs. 24 and 25. Electron micrographs from the abraded and unabraded zones respectively of an aluminium single crystal. 5% extension. Polymerization replicas. $\times 10\,000$ Fig. 26. $\times 15\,000$ Fig. 27. $\times 15\,000$ Figs. 26 and 27. Electron micrographs from the abraded and unabraded zones respectively of a copper single crystal. 5% extension. Polymerization replicas. $\times 15\,000$ [Figs. 24 and 25 are reproduced from *Philosophical Magazine*.]



Fig. 29. Al-4% Cu aged 3 hours at 190°C showing selective precipitation on a slip band. $\times 15\,000$

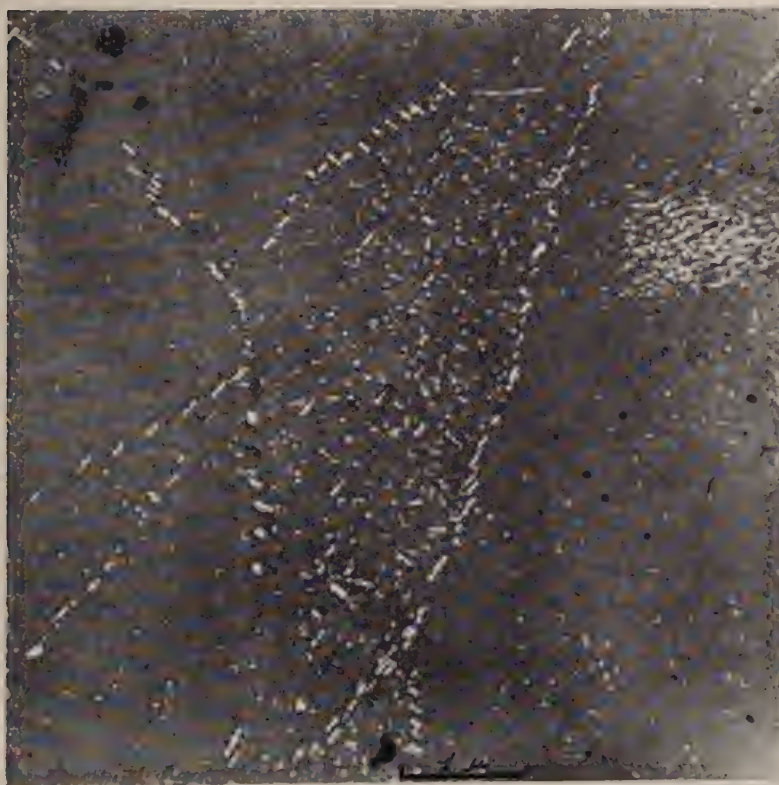


Fig. 30. Al-4% Cu aged 12 hours at 150°C showing selective precipitation on sub - grain (polygon) boundaries. $\times 15\,000$

[Figs. 29 and 30 by R. Castaing and A. Guinier (1949)
and are reproduced by courtesy of the editors of *Comptes Rendus de l'Académie des Sciences*.]

SLIP BAND PHENOMENA

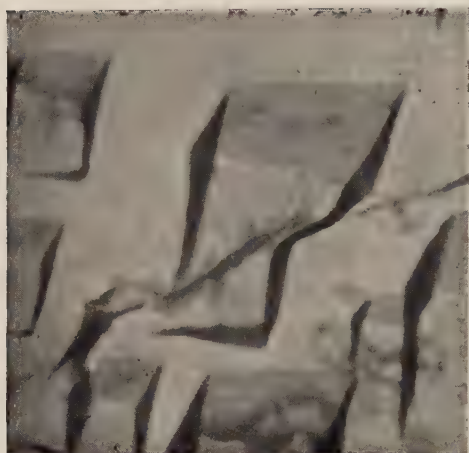


Fig. 33. Fine slip lines on both sides of ordinary slip bands. $\times 25\,000$

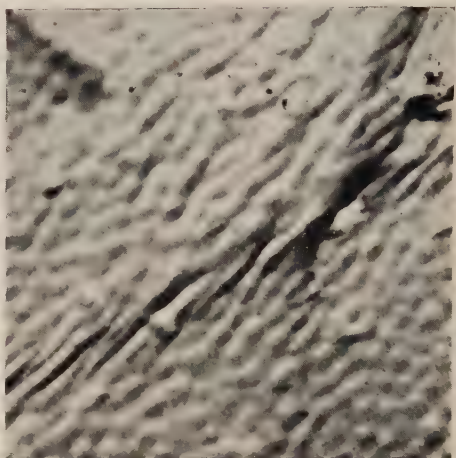


Fig. 34. Fine slip lines on both sides of ordinary slip bands. $\times 50\,000$



Fig. 52. Behaviour of slip bands at intersections with kink-bands. $\times 25\,000$



Fig. 53. Behaviour of slip bands at intersections with kink-bands. $\times 25\,000$

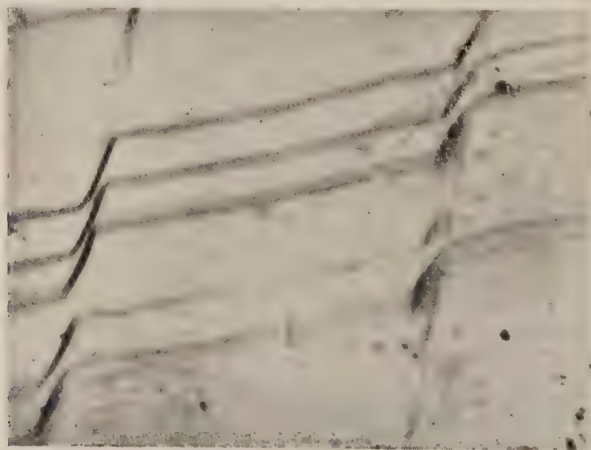


Fig. 55. Slip bands formed at -180°C faulted by other slip the direction of which lies almost in the free surface. About 80% deformation. $\times 15\,000$

[Fig. 55 is reproduced by courtesy of the *Institute of Metals*.]

SLIPLESS FLOW

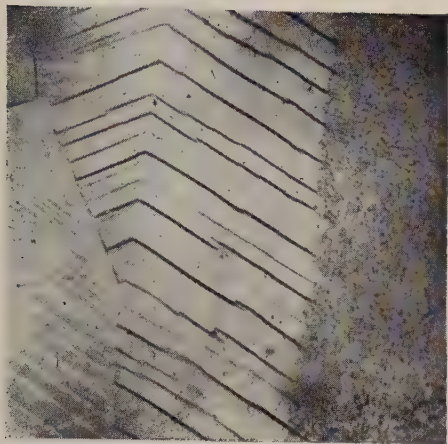


Fig. 35. Slip bands stopped at the boundary of the internally oxidized zone of a Cu-Al alloy. Light micrograph $\times 1\,500$.

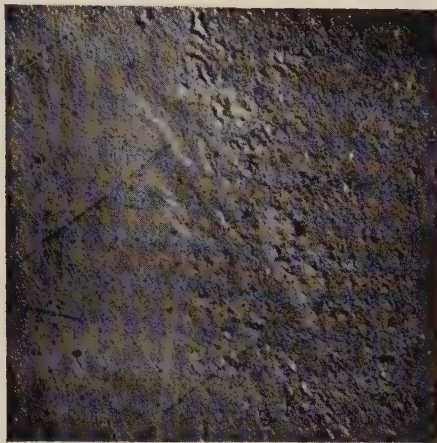


Fig. 36. As fig. 35. Electron micrograph from polymerization replica. $\times 5\,000$

[Figs. 35 and 36 by *D. W. Dewhirst*.]



Fig. 37. Al-7% Mg alloy. Solution treated: slip bands visible after 5% extension. $\times 1\,000$

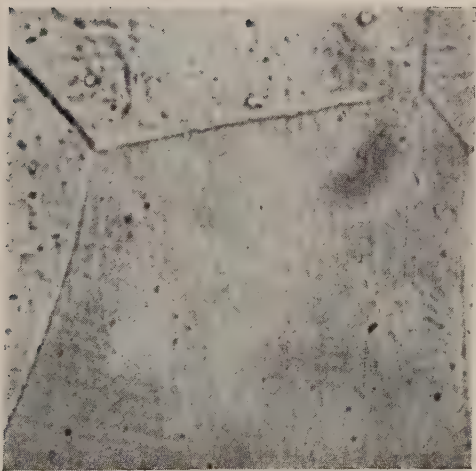


Fig. 38. Al-7% Mg alloy. Aged 2 days at 200°C : no slip visible after 5% extension. $\times 1\,000$

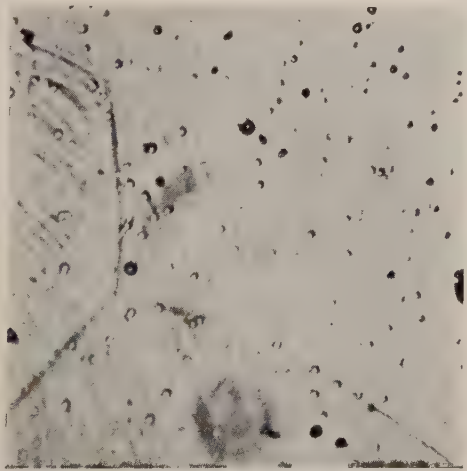
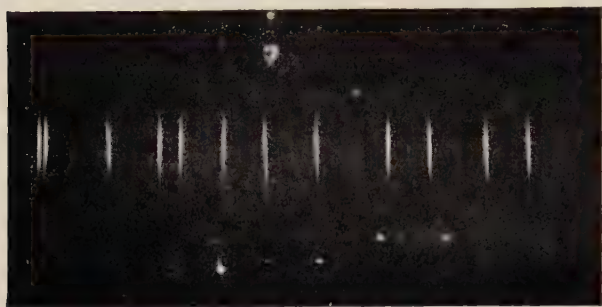


Fig. 39. Al-7% Mg alloy. Aged 1 day at 200°C : some slip is faintly visible after 5% extension. $\times 1\,000$

[Figs. 37, 38, 39 are by *C. Edleacu* and are reproduced by courtesy of the *Institute of Metals*.]

SURFACE PHENOMENA ON SOLIDS



[E. N. da C. Andrade and L. C. Tsien.]

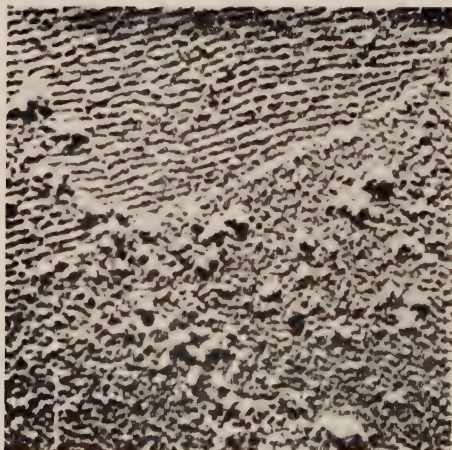
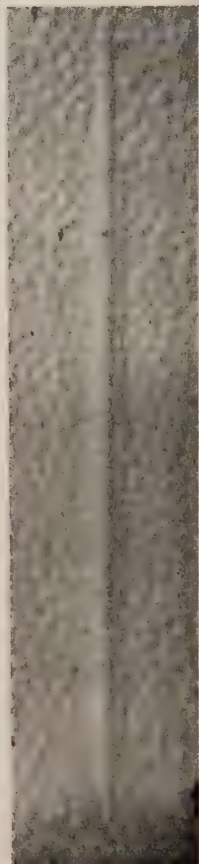
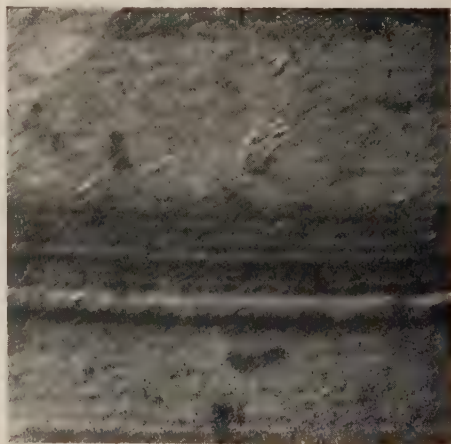
Fig. 42. Griffiths cracks on a quartz tube made visible by 'development' in sodium vapour. $\times 30$ Fig. 44. Aluminium surface showing slip band. Replica by the polymerization process shows both fine structure and micro-etch. $\times 25\,000$ Fig. 45. Change in character of micro-etch structure at a grain boundary in aluminium. Oxide replica heavily shadowed with gold-palladium. $\times 25\,000$ Fig. 43. Crack on toughened glass. Electron micrograph made by pressing polished aluminium foil against the glass, then oxidizing the aluminium and using the oxide film as a replica. The orange pattern structure belongs to the aluminium. $\times 35\,000$ Fig. 47. Micro-etch structure on aluminium $\{100\}$ surface parallel to, and similar in appearance to, the fine structure in a slip band. Oxide replica shadowed with gold-palladium. $\times 25\,000$ [Figs. 43, 44 and 47 are reproduced by courtesy of the *Institute of Metals*.]



Fig. 56. Under reversed stresses the fine steps in slip bands do not all go the same way. See fig. 57. Oxide replica, shadowed. $\times 20\,000$



Fig. 70. Fine slip at the edge of a minute scratch on aluminium. Oxide replica. $\times 10\,000$



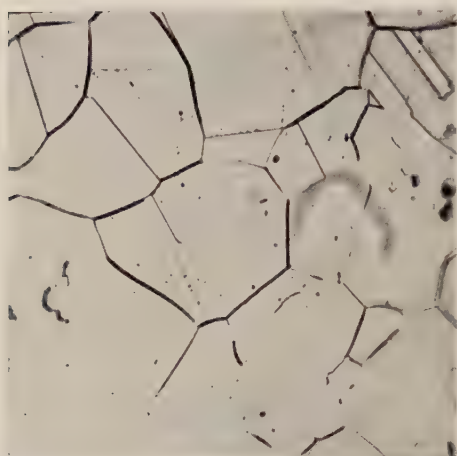
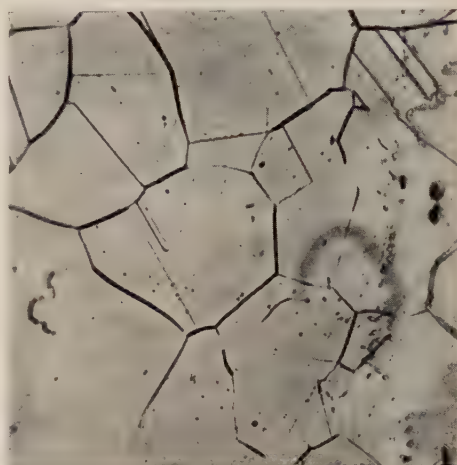
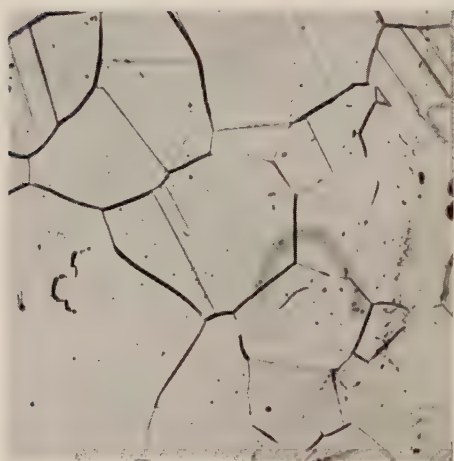
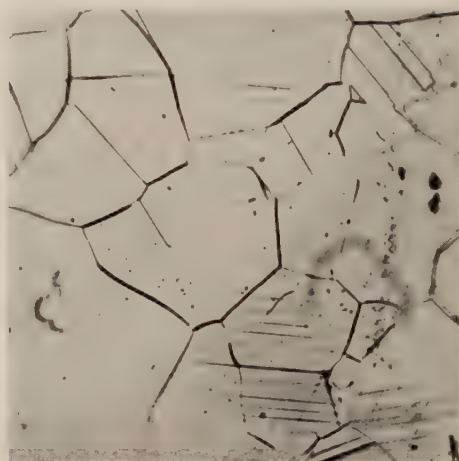
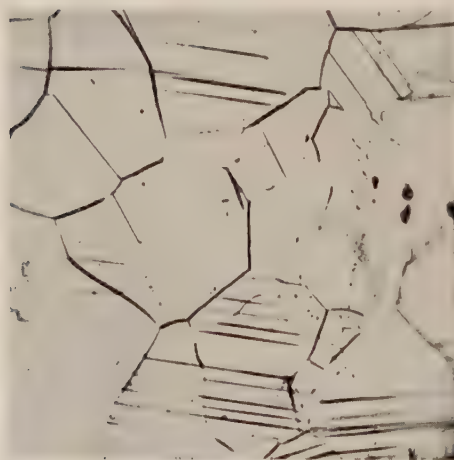
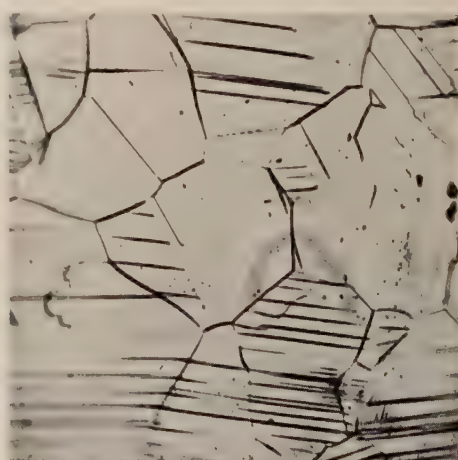
Fig. 71. A scratch perpendicular to the expected direction of slip-bands has little effect on them. $\times 100$



Fig. 72. When a scratch is made parallel to the expected direction of slip bands, there is a slip free region on either side of it. $\times 100$

[Figs. 71 and 72 by H. Nishimura and J. Takamura and are reproduced from *Memoires of Kyoto University*.]

SLIP BANDS FORMED BY ALTERNATING STRESSES

Fig. 58. Nickel 0 cycles. $\times 400$ Fig. 59. Nickel 5 000 cycles. $\times 400$ Fig. 60. Nickel 10 000 cycles. $\times 400$ Fig. 61. Nickel 25 000 cycles. $\times 400$ Fig. 62. Nickel 50 000 cycles. $\times 400$ Fig. 63. Nickel 100 000 cycles. $\times 400$

[Figs. 58, 59, 60, 61, 62, 63 by A. G. Duce.]

SLIP BANDS FORMED BY ALTERNATING STRESSES

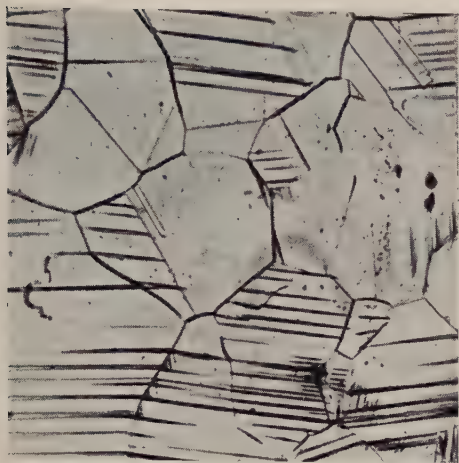


Fig. 64. Nickel 200 000 cycles. $\times 400$

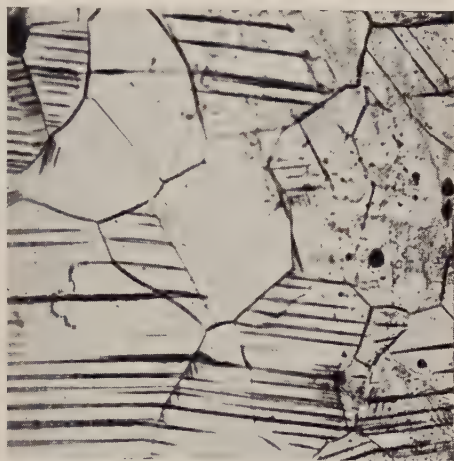


Fig. 65. Nickel 270 000 cycles. $\times 400$

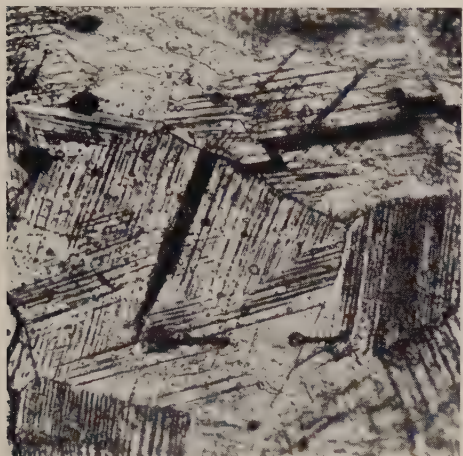


Fig. 66. Nickel after 270 000 cycles. Part of the main fracture. $\times 400$

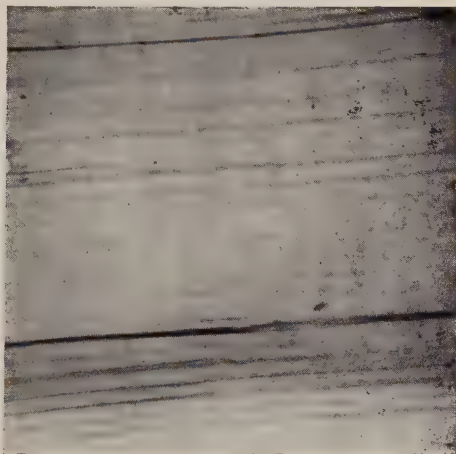


Fig. 67. Aluminium 5 000 cycles. Electron-micrograph. $\times 8\,000$

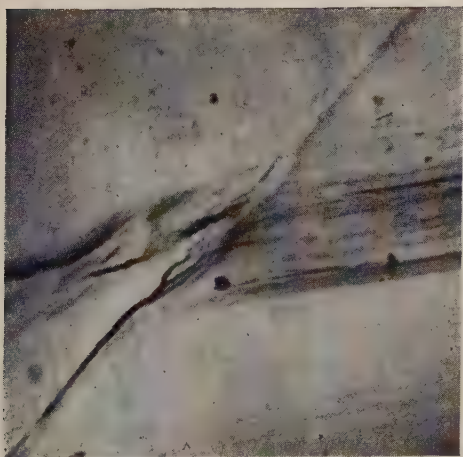


Fig. 68. Aluminium 5 000 cycles. Electron-micrograph. $\times 8\,000$



Fig. 69. Magnesium 70 000 cycles (after fracture). $\times 350$

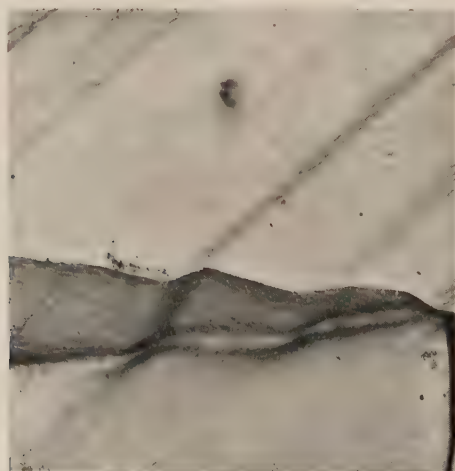
Figs. 64, 65, 66, 67, 68, 69 by A. G. Duce.]

SLIP BANDS ON ALUMINIUM DEFORMED AT VERY HIGH STRAIN RATES



Fig. 76.

Resolution of a slip band.

 $\times 20\,000$ Fig. 77. A field of closely spaced slip. $\times 10\,000$

Figs. 76 and 77 are from single crystals deformed 4% at a strain rate of 100 per sec. Both are electron micrographs from oxide replicas.

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